An Isotopic And Anionic Study Of The Hydrologic Connectivity Between The Waimakariri River And The Avon River, Christchurch, New Zealand

University of Canterbury 2015

A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in Engineering Geology at the University of Canterbury

By

Ryan Tutbury

ABSTRACT

The Waimakariri-Avon River system is an important component of the Christchurch aquifer system and has been identified as one of, if not the, primary groundwater flow path. The Waimakariri-Avon River system is ideally suited to geochemical tracing of surface water-groundwater interaction and while many past studies have been undertaken to characterise this system, in terms of its geochemistry and physical hydrogeological components, there is still a large amount of uncertainty as to how long it takes for groundwater to flow from the Waimakariri River, through the Waimakariri-Avon River groundwater system, to the springs that feed the Avon River. The primary goals of this thesis were to;

1) Constrain the residence time of groundwater connecting the Waimakariri-Avon River groundwater system using stable oxygen and hydrogen isotopes and analysis of anionic concentrations of: chloride, fluoride, nitrate, nitrite, bromide and sulfate,

2) Provide additional evidence of a hydrological connection between the Waimakariri River and the Avon River systems,

3) Present observations of the stable isotopic and anionic response of surface water to rainfall events,

4) Identify stable isotopic and anionic surface water variation along the Waimakariri-Avon River system, and establish the reasons for these.

This study presents the use of natural isotopic and anionic tracers to characterise the residence time of the groundwater that flows between the Waimakariri and Avon Rivers, by sampling surface water and meteoric water at sites that are part of the Waimakariri-Avon River system. 375 samples were collected from 10 surface water and 4 rainwater sites distributed across the Waimakariri-Avon River surface water-groundwater flow path between March 5th and August, 2014. Additionally the study provides further stable isotopic evidence of the connection between the Waimakariri and Avon Rivers, as well as presents the variability of surface water chemistry in response to rainfall events. Identification of

isotopic and anionic variation along the Waimakariri-Avon River system, by surface water sampling, was also conducted to establish the probable causes of observed variations.

This study found that the use of large rainfall events, as natural tracers, was not conclusive in establishing the groundwater residence time of the Waimakariri-Avon River system within the 4.5 month sampling period available. Surface water sampling provided further evidence in support of past studies that have determined an isotopic connection between the Waimakariri River and the Avon River with mean stable isotopic values for the Waimakariri River (-8.85‰ $\delta^{18}O$ and-60.65 δD) and Avon River (-8.53‰ $\delta^{18}O$ and -58.72 δD) being more similar than those of locally derived meteoric water (-5.48‰ $\delta^{18}O$ and -35.13 δD). Observations of surface water chemistry variations thorough time determined and identified clear responses to rainfall events as deviations from baseline values, coinciding with rainfall events. Isotopic variation along the Waimakariri-Avon River system was shown to reflect Waimakariri River derived shallow groundwater with the contributions from rainwater increasing with increased proximity to the Avon River mouth.

Anionic profiling of the Waimakariri-Avon River system identified increasing concentrations of chloride, nitrate, sulfate, nitrite and bromide, relative to the Waimakariri River, with increased proximity to the Avon River mouth. Fluoride concentrations were identified in lower concentration, relative to the Waimakariri River, with increased proximity to the Avon River mouth. Fluoride and nitrite concentrations were attributed predominantly, if not entirely, to an atmospheric source as mean concentrations were greater in meteoric waters by a factor of at least 2, compared to surface water samples. Chloride and bromide have been attributed to possible salt water mixing as a result of the interaction of upwelling deeper groundwater with the marine and estuarine sands beneath the upper unconfined aquifer, that act as a confining layer within the Christchurch aquifer system. Nitrate and sulfate concentrations have been attributed to potential fertilizer usage and past land-use impacts.

A significant step-change increase in chloride, bromide, nitrate and sulfate concentrations was observed between the surface water sample sites at Avonhead Park and the University of Canterbury. The step-change coincides with the boundary of the upper confining layer within the Christchurch aquifer system, and explains the increases in chloride and bromide

concentrations. It also suggests a widely distributed source area as concentrations do not become diluted at the Avon River site, at Hagley Park, , which would be expected from the addition of other tributaries, if they did not have similarly high chloride and bromide concentrations. The area between these two sites has also been identified by Environment Canterbury as potentially impacted by past agricultural land-use practices and may explain the increases in nitrate and sulfate concentrations.

ACKNOWLEDGEMETS

First and foremost I would like to thank my supervisors Travis Horton and David Bell. In particular Travis, for enduring my endless pestering and providing me with the topic on which to base this thesis and insight into the world of stable isotopes in hydrology. Also for the answers to many of my questions, processing the numerous water samples (to gain their stable isotopic compositions) and discussions regarding 'what on earth my data actually meant'. Thanks to David Bell for being an editing magician and providing critical feedback during the final stages of my thesis.

I would also like to thank the geology staff with special regards to Kathy, Janet, Janet, Rob, Sacha, Matt, Mike and Pat. Rob, for working with me to gain access to the roof of the library in order to place my rainwater collector, the view from the top is truly stunning on a clear day. Kathy, the Janets, Mike and Sacha for arranging the use of the department vehicles, lab equipment and general enquiries. Matt Cockcroft for his assistance in preparing samples and using the departments ion chromatograph, a machine that till this day I still have little idea as to how it actually works. Finally to Pat who helped get me paid for my time spent tutoring or claiming scholarship funds. I must also thank the Mason Trust Fund to whom I owe thanks for providing the funds used to conduct this thesis.

Finally all my family, friends and colleagues whom endured and supported me during this seemingly short 12 months, be it during the whole time, or for various parts. In particular to Tori, who helped me with early morning and late night water sample collections. Grace, Jo, Mitch and Andrew who listened to countless vents of frustration and proved numerous laughs and discussions within the office and on our coffee breaks, best of luck to you all and I am hoping to see you all at the December graduation. Lastly Chloe, for supporting me especially during the final stages. To all those whom I have forgotten my apologies, there are just too many to remember at this time.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 PROJECT BACKGROUND

The primary aim of this thesis is to establish the residence time of the groundwater connecting the Waimakariri River to the spring-fed tributaries of the Avon River. The Waimakariri River's main recharge source area is in the Southern Alps of the South Island of New Zealand (Figure 1.1). The river then flows onto the Canterbury Plains in a south and east-ward direction before discharging into the Pacific Ocean.

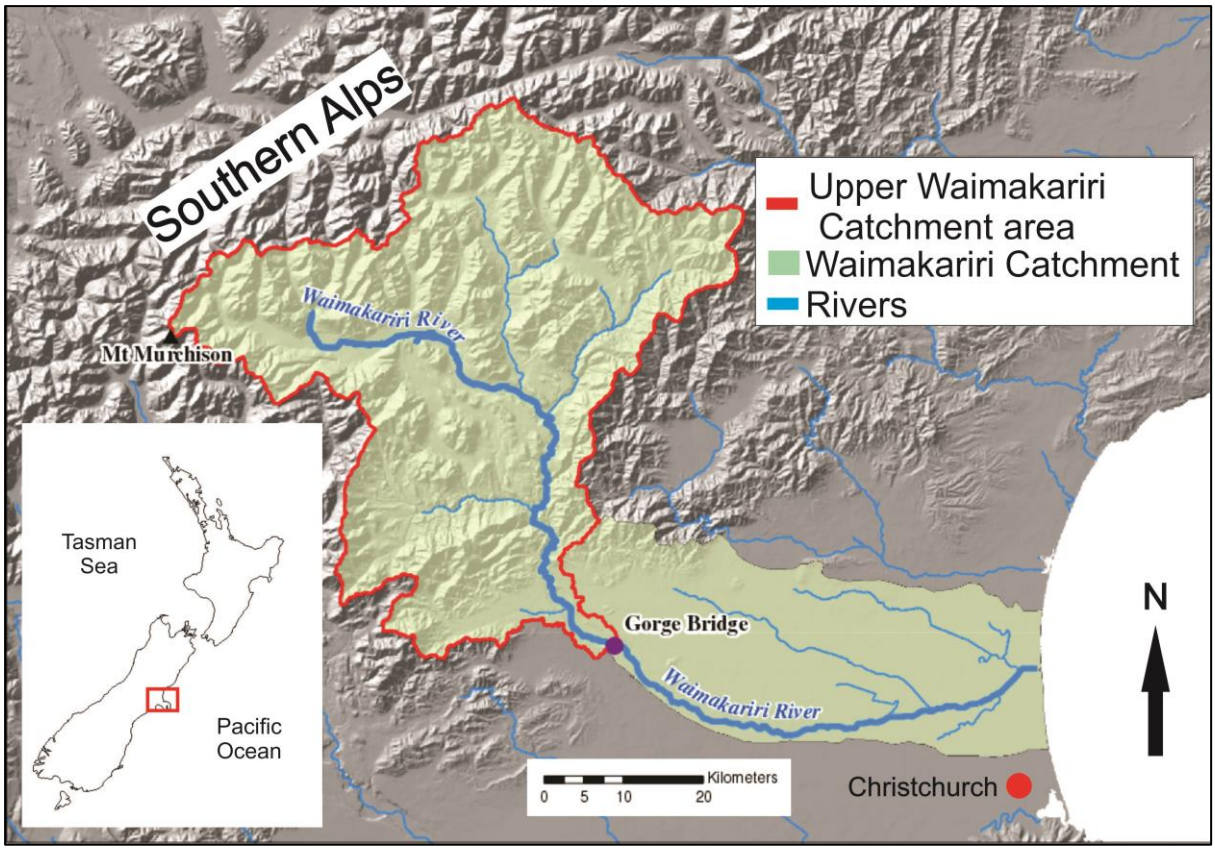


Figure 1.1: Waimakariri River catchment area (modified from Lu, 2009).

The Waimakariri River is an important component of the groundwater system beneath Christchurch, as it is the primary recharge source for the groundwater beneath the city. The water from the Waimakariri River percolates into the underlying gravels of the Canterbury Plains and flows in a generally eastward direction toward the city. Here the groundwater enters into a system of confined and unconfined aquifers where it flows seaward and is extracted for domestic and industrial use (Figure 1.2).

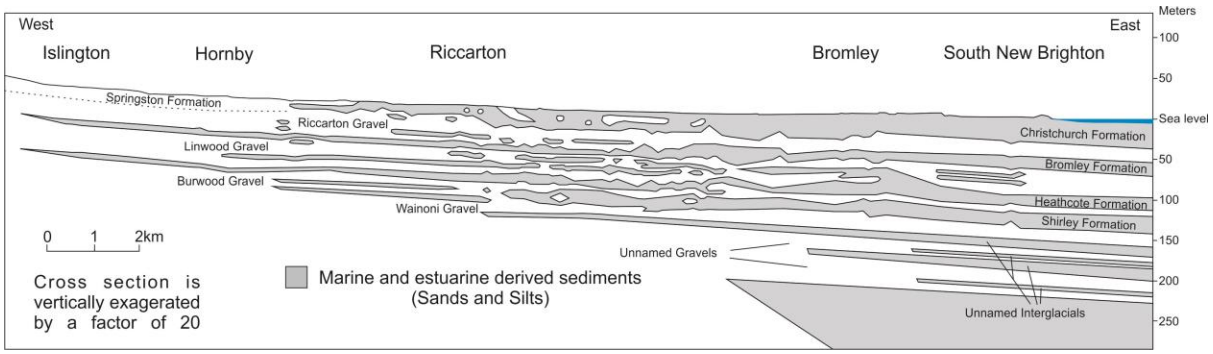


Figure 1.2: Stratigraphy of interfingered aquifer gravels and confining marine/estuarine sediments beneath Christchurch (modified from Brown & Weeber, 1992).

Natural springs form where 'holes' in the confining layers have enough confining pressure to enable groundwater to flow up to the surface. The springs presented in figure 1.3 all act as tributaries for the main river channel, the Avon River. As it is the Waimakariri River that recharges the groundwater, which supplies the baseline flow for the Avon River, there is an inherent connection between the two river systems linked by the groundwater that flows beneath the surface. Studying this system enables more accurate estimates into the flow rates of groundwater between these two rivers, as well as providing a basis in determining groundwater recharge rates of the aquifers beneath the city of Christchurch.

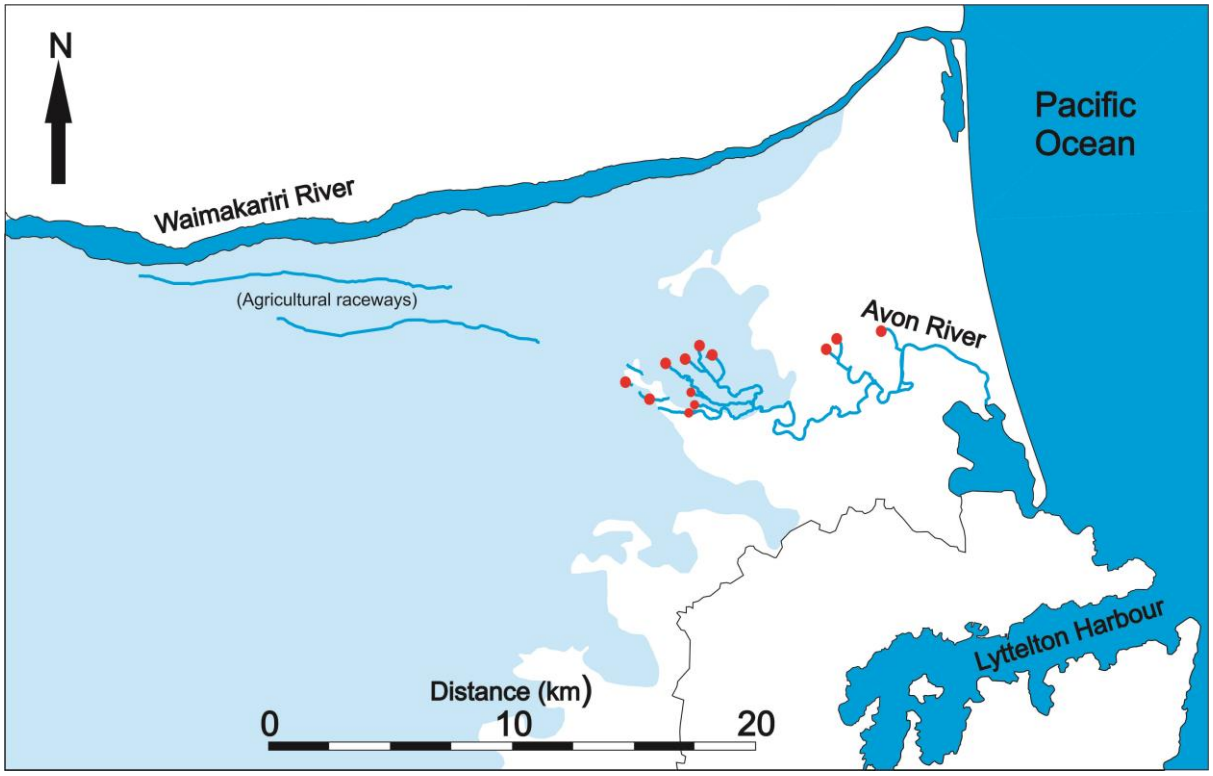


Figure 1.3: Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system. Blue lines and red dots indicate surface water flow paths and known spring sites, respectively, of Avon River tributaries.

1.2 THESIS METHODOLOGY

In order to determine the residence time of the groundwater within the Waimakariri-Avon River system, surface water samples were collected at sites part of the system, with the addition of rainwater samples from local rainfall events. The sites were chosen based on: the presence of a constant supply of surface water, land that was publicly accessible and also down gradient of the Waimakariri River in terms of the regional groundwater potentiometric surface (Figure 1.4).

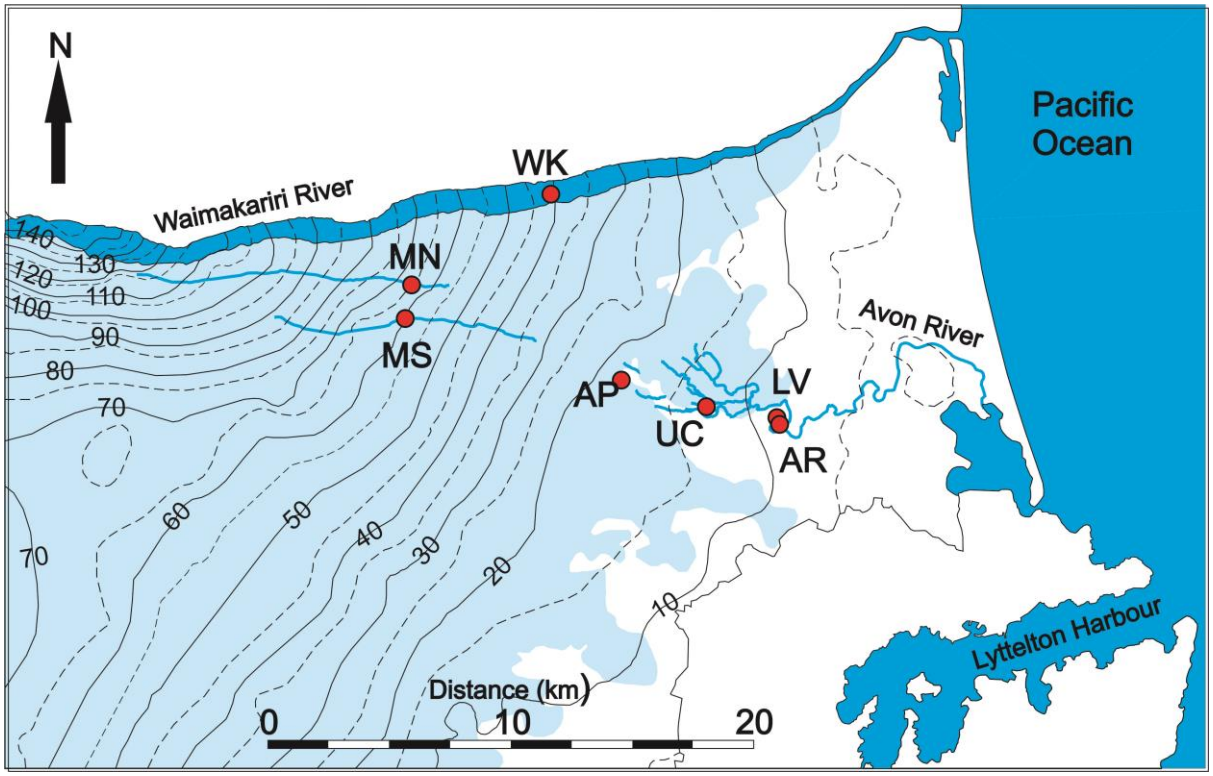


Figure 1.4: Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system. Contours indicate depth to the water table with groundwater flow in the direction perpendicular to contour lines. Blue lines indicate surface water flow paths. Red circles indicate sample sites with accompanying site code.

Two large rainfall events in March, 2014 were used as natural isotopic tracers to be tracked through the Waimakariri-Avon River system. The two large rainfall events were isotopically distinct from both mean local rainwater and local ground and surface waters. The rainfall events had durations longer than 24 hours and sufficient rainfall volumes to alter the Waimakariri River surface waters long enough to ensure uptake into the groundwater system. Surface water samples were collected weekly for 4.5 months (March-July, 2014) following the first rainfall event, March 5th, 2014, as well as daily at the University of Canterbury. Rainwater samples were collected from the two March, 2014 rainfall events as well as rainfall events during the sampling period.

Samples were analysed for their isotopic compositions and anionic concentrations to characterise individual rainfall events. This enabled individual events to be identified as they flowed through the Waimakariri-Avon River system, as well as determining the baseline compositions and concentrations of the rain, ground and surface waters. By analysing

temporal changes in isotopic compositions and anionic concentrations at consistent time intervals, it was possible to identify rates at which rivers responded to rainfall events and their duration within the groundwater-surface water system. Comparing isotopic compositions and anionic concentrations between the Waimakariri River and the Avon River contributed to previous studies and identified an area of potential influence that is altering anionic concentrations within the groundwater and along the course of the Avon River.

1.3 PREVIOUS INVESTIGATIONS

There have been many past investigations conducted on the Waimakariri-Avon River system, as well as studies of the rivers themselves. The presence of the aquifer system beneath Christchurch was first hypothesised in the 1860s. Sir Julius Von Haast (1879) issued a report in 1863 at the request of the City Council Chairman, Hon. John Hall, into the practicability of supplying water to Christchurch by means of artesian wells. Although Von Haast advised against it, concluding that it would be easier to acquire water from surface water sources (Avon and Heathcote Rivers), he postulated that there existed a layered gravel structure beneath the city with good artesian wells likely to be obtained from drilling the deeper gravel layers (Brown & Weeber, 1992). This hypothesis was verified when numerous wells were drilled in order to supply fresh water to the city.

One of the first studies conducted in Canterbury compiling isotopic compositions and chemical concentrations of surface and groundwater was conducted by Taylor et al. (1989) in an attempt to characterise the origins of the groundwater. The study identified that $\delta^{18}O$ values could be attributed to the waters' origins (Table 1.1).

Water Origin	$\delta^{18}O$ Value (‰) (V-SMOW)
Meteoric	**>-7.50**
Meteoric + Groundwater	**-7.50 to -8.50**
Groundwater	**<-8.50**

Table 1.1: Table of expected $\delta^{18}O$ values for water origins (Taylor et al. (1989).

Regional potentiometric groundwater levels suggested that the Christchurch aquifer system was recharged not only by rainwater, but also upwelling groundwater from deeper aquifers and Waimakariri River derived groundwater. Taylor et al. (1989) went further to say that Waimakariri River derived groundwater took no longer than one year to reach the boundary of the confined aquifer zone, 10km away (refer: Figures 1.3 & 1.4).

The GNS publication, 'Geology of the Christchurch Urban Area', compiled by Brown and Weeber (1992), gives a thorough explanation and interpretation of the hydrogeology beneath Christchurch. Included is the interpreted geological stratigraphy and history of the Christchurch area. Brown and Weeber (1992) also provide insight into the hydrology of the area including approximate ages of groundwater, as well as their origin, and groundwater flow pathways from past studies conducted in Christchurch and the wider area.

Physical properties of the groundwater system were assessed in a studies conducted by Callander et al. (2005) and White (2009). Callander et al. (2005) modelled the groundwater flow rate, using groundwater flow software, and produced groundwater residence times for various groundwater wells in the city. Callander et al.'s (2005) findings determined residence times far greater than that of Taylor et al.'s (1989) study by a factor of 3 or more. White (2009) identified potential groundwater flow paths by which the dominant recharge from the Waimakariri River reaches the Avon River springs via a past channel of the Waimakariri River.

A Masters thesis carried out by Blackstock (2011), of the University of Canterbury, investigated the isotopic signatures of ground, surface and precipitation waters. Blackstock concluded that the groundwater was the result of alpine derived rainfall with minor contributions of local precipitation events, confirming conclusion made by Taylor et al. (1989). He also noted the significant variation in local precipitation events and was able to characterise their origins based on their isotopic signature.

White et al. (2012) investigated the outflow of water from a section of the Waimakariri River into the underlying river bed. His study found there was significant outflow into the adjacent river gravels and deduced that the basal flow of the many springs in Christchurch are fed by this outflow, with rainfall volumes being unable to account entirely for the discharge

volumes observed at the spring sites. Measurements of nitrogen concentrations within the main flow of the Waimakariri River were also determined and found to be <0.1mg/l.

Another Masters thesis from the University of Canterbury, by Cronin (2012), characterised the Waimakariri, Avon and Heathcote Rivers using oxygen, hydrogen and carbon isotopes, as well as their anionic compositions with regards to: chloride, fluoride, bromide, nitrate, nitrite and sulfate. Cronin's study identified close similarities in isotopic and anionic signatures between each of the three surface water bodies providing further evidence of the connection between the Waimakariri and Avon Rivers. It is the role of this thesis to further characterise aspects of the Waimakariri-Avon River system, in particular that of the residence time of the water flowing in this system.

1.4 THESIS AIMS

The primary objective of this thesis is to constrain the residence time of groundwater connecting the Waimakariri-Avon River groundwater system using stable oxygen and hydrogen isotopes and analysis of anionic concentrations of: chloride, fluoride, nitrate, nitrite, bromide and sulfate. Previous work by Taylor et al. (1989), Brown and Weeber (1992), Blackstock (2011)and Cronin (2012) identified the isotopic connection between the Waimakariri and Avon River water bodies, and past studies, like that of Brown and Weeber (1992,) Callander et al. (2005) and White (2009), have identified preferential subsurface flow paths.

Additional objectives of this thesis are:

- To provide additional evidence of a hydrogeological connection between the Waimakariri River and the Avon River systems,
- To present observations of the stable isotopic and anionic response of surface water to rainfall events,
- To identify stable isotopic and anionic surface water variation along the Waimakariri-Avon River system, and establish the reasons for these.

1.5 THESIS FORMAT

This thesis is divided into 6 chapters;

Chapter 2 provides concepts and information about the processes and controls on physical and geochemical aspects of hydrogeological processes relating to this study,

Chapter 3 gives an overview of the study area and the location of the sites that were used for sample collection, as well as describing the methods and means of analysis that were used in sample collection and sample analysis,

Chapter 4 presents the results of the sample analysis that were of significance,

Chapter 5 discusses the results,

Chapter 6 summarises the thesis with final conclusions and implications of the study and offers potential focuses of future research for groundwater studies.

CHAPTER 2: HYDROGEOLOGICAL CONCEPTS AND PROCESSES

2.1 INTRODUCTION

This chapter presents an overview of: the hydrologic cycle, the connections between hydrologic reservoirs (components of the hydrologic cycle), and the processes governing the major volumetric fluxes between components within the cycle, with a focus on the surface and groundwater reservoirs within the hydrologic cycle. The constraints and controls that geology has on surface and groundwater are introduced and how they can be used to estimate groundwater flow rates and residence times (Fetter, 2001; Heath, 1983; Kazemi et al., 2006).

The use of stable isotope analysis is used in many applications as a conservative tracer within ground and surface water systems (Taylor et al, 1989; Blackstock, 2011). Stable isotope variations are well understood within the hydrologic cycle, in particular meteoric water (Sharp, 2007). Primary causes for variations in isotopic ratios are the origin of vapour mass sources, latitude and temperature (Clark & Fritz, 1997; Kenndall & McDonnell, 1998). Anion concentration analysis of chloride, bromide, nitrate, fluoride, nitrite and sulfate can be used to identify natural processes and anthropogenic influences on ground and surface waters (Fetter, 1999; Avery et al., 2001). These influences and processes generally occur as a result of fertilizer usage, sewerage leakage, water-rock interactions or salt water intrusion. With knowledge of the chemistry, and the point in time where a tracer enters into a groundwater system, it is possible to measure aspects of the groundwater flow rate and residence time within a system. So I have used a combination of stable isotope and anion concentration analyses in order to constrain the residence time of the groundwater in the Waimakariri-Avon River system.

2.2 THE HYDROLOGIC CYLCE

2.2.1 OVERVIEW

The movement of water through the earth system is often represented by a simplified diagram, termed the hydrologic (water) cycle. The hydrologic cycle is the continuous, unsteady circulation of the water resource within the earth system. The cycle is dynamic in

that the quantity and quality of water varies spatially, given geographic location, as well as greatly with time (Walesh, 1989). Figure 2.1 illustrates the relative percentages of earth's water resource and divisions amongst the various reservoirs.

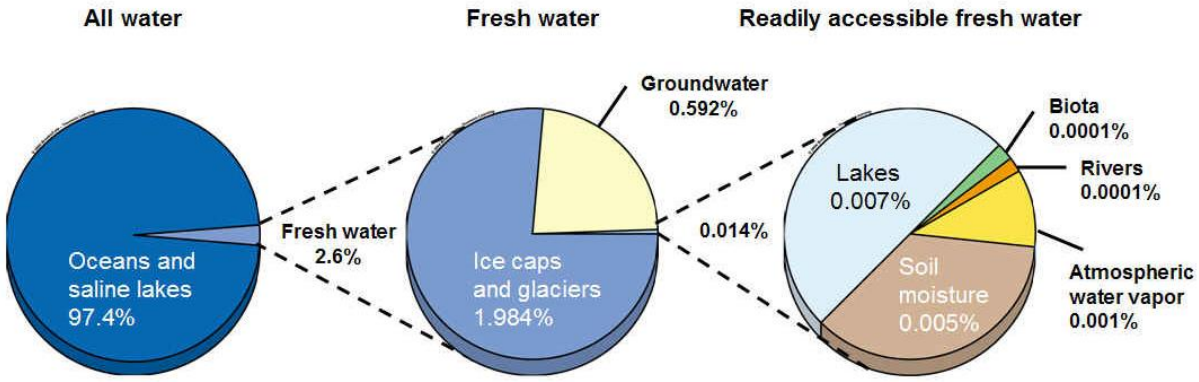


Figure 2.1 : Allocation of earth's water resources (CUNY, 2011).

Figure 2.2 depicts the water cycle, illustrating the various reservoirs of water within the earth system and the processes connecting them. As shown, all of the terrestrial derived water is recharged, almost exclusively, by precipitation (rainfall, hail, sleet and snow). It is from this that freshwater is derived for day-to-day use.

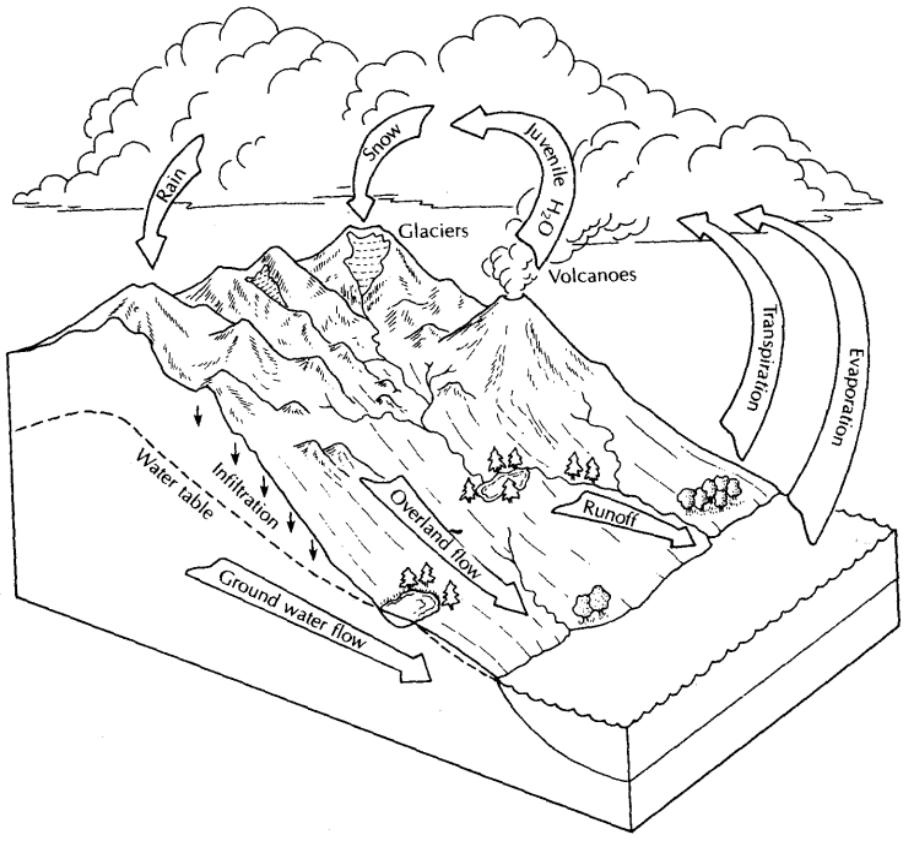


Figure 2.2:

A simplified diagram of the hydrologic cycle (Fetter, 2001).

2.2.2 HYDROLOGIC FLUXES

Accurately calculating fluxes between the different hydrologic reservoirs is one of the challenges faced by many countries and communities today. One simple method is the use of a fundamental mass balance equation, commonly used when determining the flux of water from one hydrologic reservoir to another, where mass is conserved (Fetter, 2001; Bowen, 1986);

$$Inflow - Outflow \pm Changes\ in\ storage = 0 \qquad Eq.\ 2.1$$

For many of the hydrologic reservoirs the equation can be expressed as;

$$P \pm E \pm \Delta S \pm Q = 0 \qquad Eq.\ 2.2$$

where P is precipitation, E is evapotranspiration, ΔS is the change in storage and Q is the discharge (Davie, 2008). There is no overall net change to the hydrologic cycle as mass is conserved.

Using this equation, as well as scientific measurements, estimates can be made as to the volume of water that is moving between each of the reservoirs and the rate of water exchange in the hydrologic cycle. Table 2.1 provides estimates of the fresh water exchange rates between the different fresh water components of the hydrologic cycle.

Hydrologic Cycle Component	Volume (km^3)	% of Fresh water (Worldwide)	Rate of Exchange (Years)
Ice sheets and glaciers	24,000,000	84.945	8,000
Groundwater	4,000,000	14.158	280
Lakes and reservoirs	155,000	0.549	7
Soil moisture	83,000	0.294	1
Atmospheric vapour	14,000	0.049	0.03
River water	1,200	0.004	0.03
Total	28,253,200	100.0	

Table 2.1: Estimated average fresh water exchange rates within the hydrologic cycle (modified from Heath, 1983).

2.2.3 THE HYDROLOGIC CONNECTION BETWEEN GROUND AND SURFACE WATER

There is often a false compartmentalisation between surface water (rivers, lakes and streams) and groundwater (subsurface water). Although it is often represented as a one-way system, with surface water percolating through the ground surface and into the groundwater system, the two are also conversely connected with groundwater contributing to some surface water bodies via springs or elevated water tables (Soliman et al., 1998). Surface water and precipitation recharge the groundwater system, but in many cases groundwater also recharges, and is the source of, water in rivers and streams (Figure 2.3).

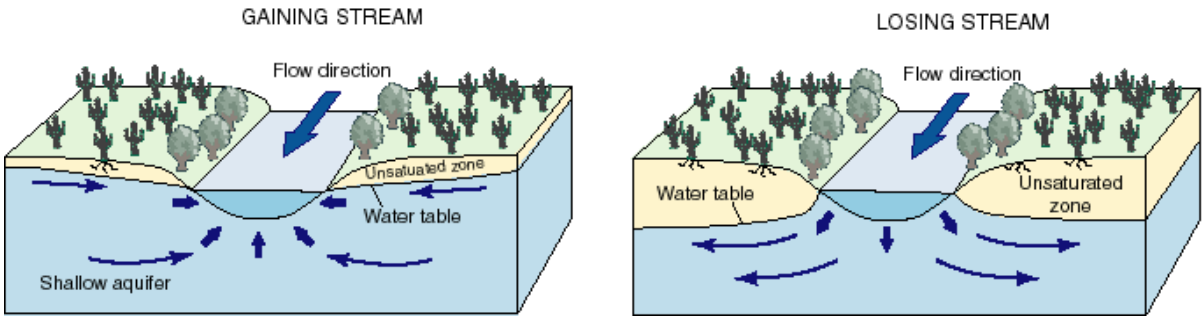


Figure 2.3: Surface and groundwater are often connected, and water can flow in either direction depending on the elevation of the stream or lake relative to the water table in the aquifer (groundwater); (Stute, 2002).

It is this relationship that should be considered, and a combined approach used when investigating surface or groundwater systems. The controls regulating the exchange of water between these two 'separate' systems are largely governed by the underlying geology and material properties.

2.3 HYDROGEOLOGICAL CONTROLS

2.3.1 BACKGROUND

Rock and soil properties, such as porosity and permeability, enable surface water and precipitation to percolate and recharge a groundwater reservoir, as well as enable groundwater to be present beneath the earth's surface. These two controls underlie the key principles that govern ground and surface water flow interactions. Structural geological features, such as fractures and bedding, may also control the presence or absence of groundwater. Coupled together, geology constrains and limits the natural flow rate of surface and groundwater flow, and the rate of exchange from one hydrologic reservoir to another.

2.3.2 POROSITY AND PERMEABILITY

Porosity is defined as the percentage of a material (in this case rock or soil) that is void of material. It is mathematically defined by the equation;

$$n = \frac{100V_v}{V} \qquad Eq.\ 2.3$$

where n is the total porosity (percentage), V_v is the volume of void space within the material, and V is the total volume of the material (Fetter, 2001).

It is within the voids, or pore space, that fluids (water and air) are present. Another important distinction for defining materials is the effective porosity. Effective porosity is the percentage of pore space, within the material, that is interconnected (Figure 2.4); (Domenico & Schwartz, 1990).

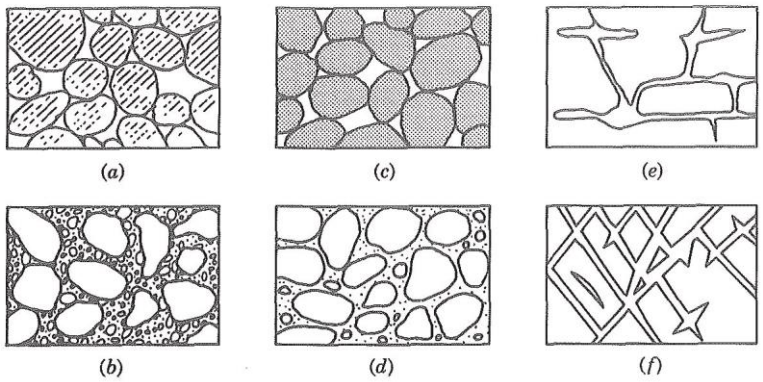


Figure 2.4: Varying examples of porosity. (a), (c), (e) and (f) display materials with high porosities, with (e) and (f) also displaying high effective porosity. (b) and (d) display materials with low porosities. (modified from Domenico & Schwartz, 1990).

It is this property that governs whether or not flow within the material can occur. The ease of flow through the material is defined in terms of hydraulic conductivity, which is a function of permeability. Material in which flow occurs more easily is defined as having good permeability, whereas material in which flow is difficult, or restricted, is defined as less permeable or having poor permeability (Fetter, 2001). A rock with high effective porosity will not necessarily have good permeability as it is the width of the connections between pores that will control the rate of flow. The wider the connections, the higher the rate of flow (Younger, 2007). Features such as fractures, joints and faults greatly increase the permeability of a material, but can have minimal effect on the effective porosity as a whole (refer: Figure 2.4). Quantifying permeability is often represented in terms of hydraulic conductivity. Hydraulic conductivity is closely related to permeability and gives a rate of flow, or velocity, of fresh water through a unit cross-section of a material. Volumes of soil or rock which exhibit good permeability, effective porosity and relatively high hydraulic conductivity are very effective at storing water and are termed aquifers.

2.3.3 AQUIFER SYSTEMS

Aquifers store groundwater and are commonly bodies of saturated rock or soil. Aquifers both store and transmit significant quantities of groundwater and are generally porous units of rock with sufficient permeability to enable groundwater abstraction or flow to springs (Younger, 2007). Aquifers are classified into two main categories; unconfined and confined

(Figure 2.5). Unconfined aquifers are those where the upper bounds of the aquifer are open to air and the water level is free to fluctuate. Unconfined aquifers are often those found close to the surface and the upper limit is often defined as the water table (refer: Figure 2.5). Confined aquifers are those that have the upper limit bounded by a confining layer. A confining layer is that of lower permeability to that of the aquifer (refer: Figure 2.5). A potentiometric surface is the imaginary level to where a given reservoir of fluid will "equalize out to" if allowed to flow and is often associated with confined aquifers, as they are usually under confining pressure (Fetter, 2001). For an unconfined aquifer the potentiometric surface is the water table (refer: Figure 2.5).

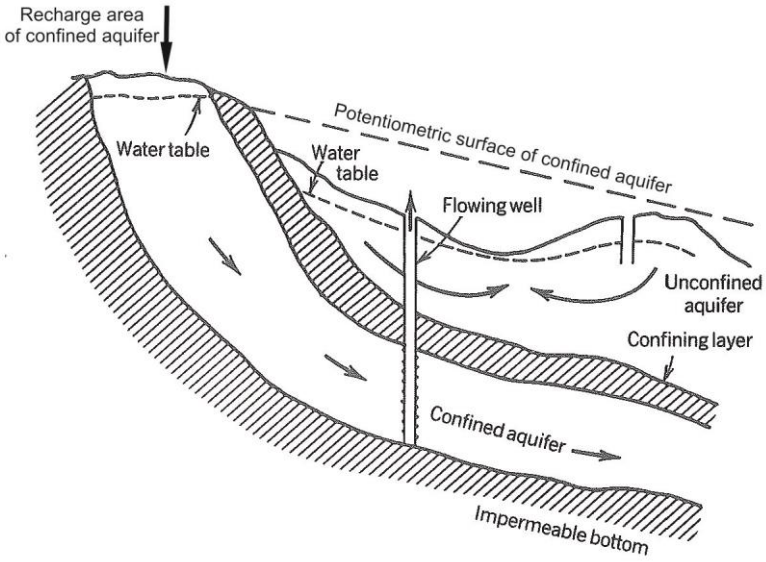


Figure 2.5:

Schematic cross section illustrating the difference between a confined and an unconfined aquifer (modified from Domenico & Schwartz, 1990).

2.3.4 TOPOGRAPHIC EFFECT AND SUBSURFACE FLOW

Topography has a recognisable effect on surface water flow. Precipitation flows down-slope into valleys, or gullies, feeding rivers and streams. Topography also has a similar effect on groundwater. Gravity drives groundwater in the direction of headloss (down-slope), toward streams or the coast, with headloss over a unit length referred to as the hydraulic gradient. Using this knowledge, groundwater flow paths can be predicted by measuring the potentiometric surface at different locations with reference to a specific datum (i.e. sea level). The use of many measurements at different locations can then be used to produce a potentiometric surface map, of a particular aquifer, showing groundwater contours, used to predict the direction of groundwater flow. Figure 2.6 presents a cross-sectional diagram

illustrating groundwater flow habits. The groundwater flow is represented in the direction perpendicular to the potentiometric contour, where the hydraulic gradient and rate of flow are the highest. This helps to identify potential sources of recharge as well as points of discharge. Instances where the water table, or potentiometric surface, intersect the land surface are where springs or seepage may occur (Heath, 1983).

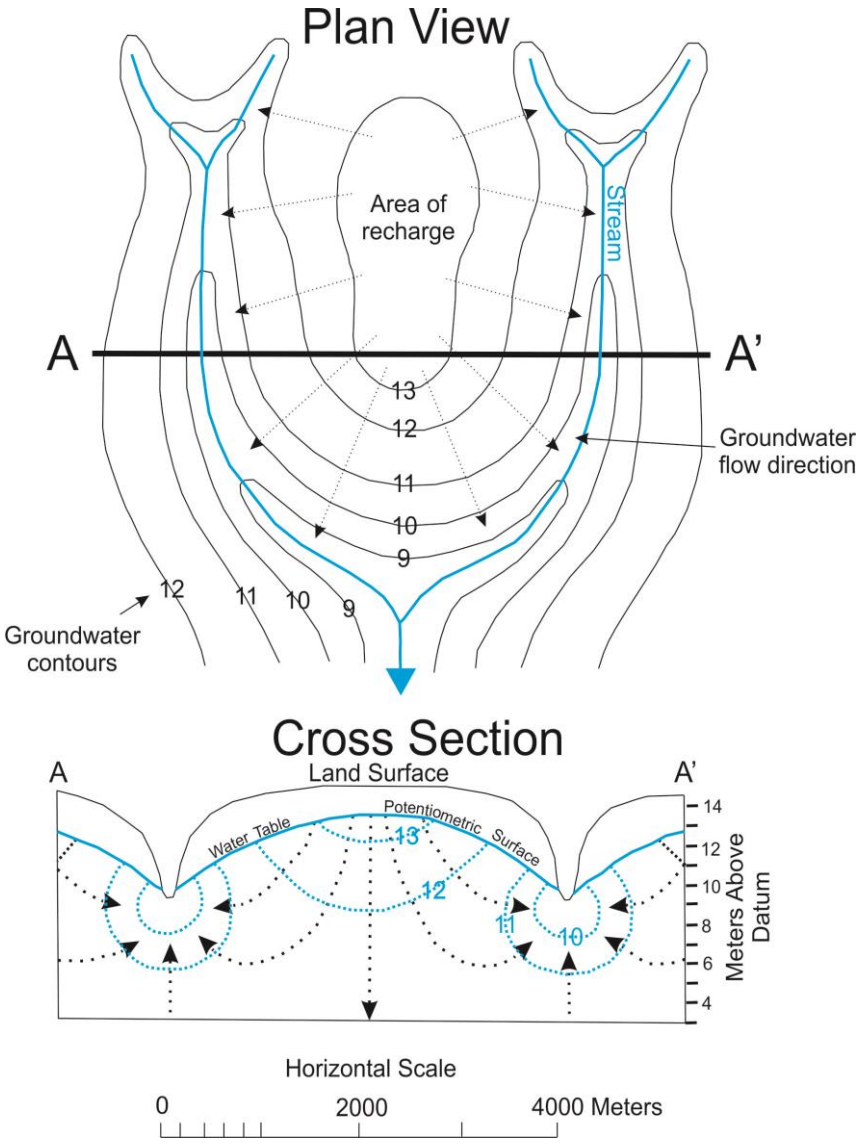


Figure 2.6: Groundwater flows from the higher potentiometric contours to the lower 5 potentiometric contours. The greatest flow rate is perpendicular to potentiometric contours. The cross section shows that vertical flow also occurs following similar principles (modified from Heath, 1983).

2.3.5 GROUNDWATER FLOW RATES AND RESIDENCE TIME

Groundwater flow rates are estimated using 'Darcy's Law', derived by Henry Darcy in 1856 (Younger, 2007). Darcy's experiment found that discharge is proportional to the difference in height of the water (hydraulic head) between the ends and inversely proportional to flow length, for a given medium, with a certain surface area (Figure 2.7); (Fetter, 2001).

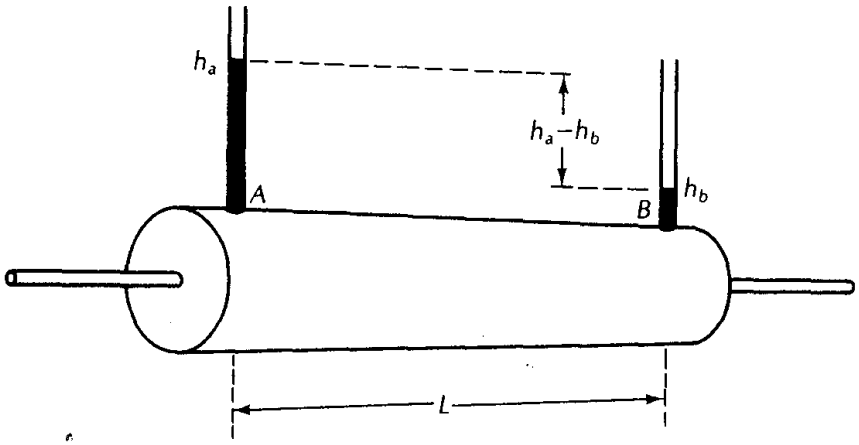


Figure 2.7: Horizontal pipe filled demonstrating Darcy's experiment. (Darcy's experiment was vertically oriented and used sand as the medium); (Fetter, 2001).

This can be expressed more simply as;

$$Q = K\ x\ i\ x\ A \qquad Eq.\ 2.4$$

where Q is the flow rate, K is the hydraulic conductivity of the medium, i is the hydraulic gradient (the change in the height of the potentiometric surface with distance), and A is the cross sectional area (Younger, 2007). Darcy's equation has since been used to quantify rates of flow into aquifers using this method.

Hydraulic conductivity is measured as a unit length per second (i.e. ms^{-1}) and varies between materials as with permeability. It has been well studied to give expected values of flow through different rock types and sedimentary deposits (Figure 2.8). While hydraulic conductivity is often represented in terms of meters per second, meters per day can be applied in cases where suitable, such as materials with low hydraulic conductivities or over great distances.

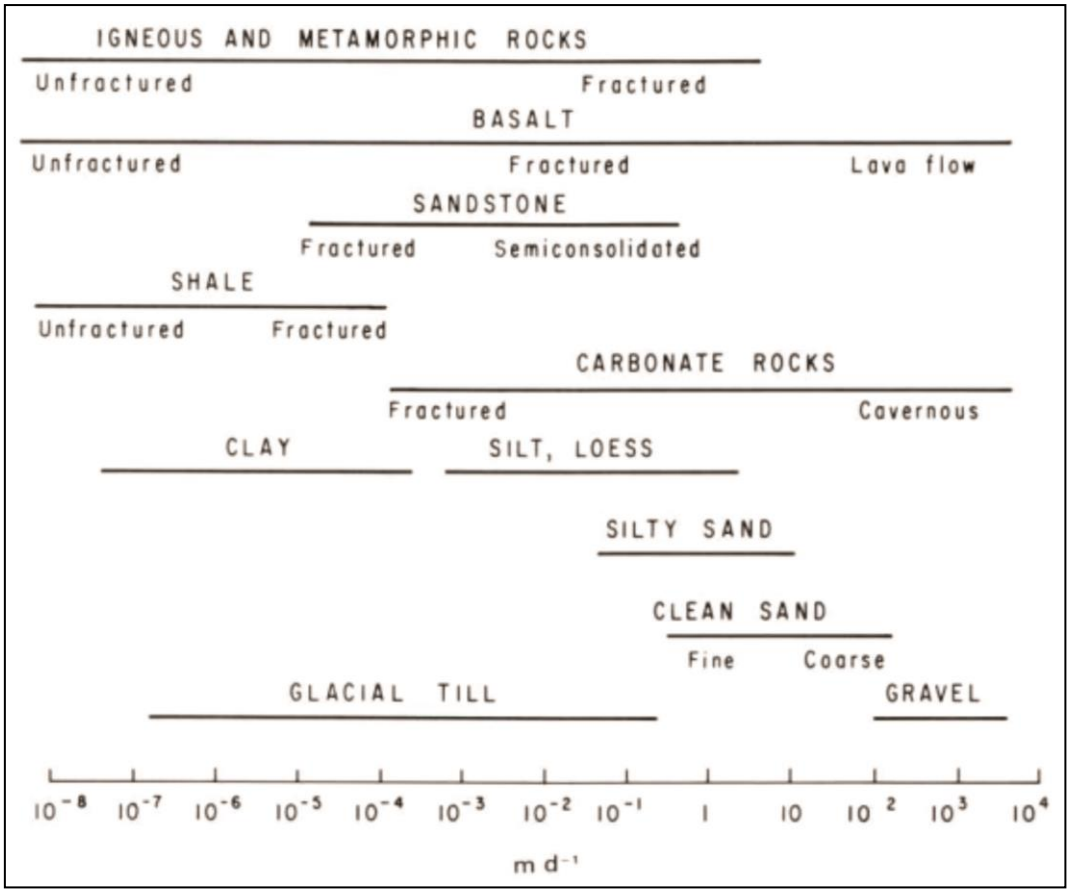


Figure 2.8: Expected hydraulic conductivities of selected rock types and sedimentary deposits in meters per day (md^{-}); (modified from Heath, 1983).

Residence time is another important aspect when considering aquifer systems. It is often used as a means of comparing discharge from the system with the rate of recharge. Residence time can be thought of as simply;

$$\tau_r = \frac{V}{Q} \qquad Eq.\ 2.5$$

where τ_r is the residence time of the reservoir, V is the volume of the reservoir, and Q is the net flux (Kazemi et al., 2006). It should be noted that if the rate of discharge is greater than the rate of recharge, the residence time will be reduced compared to that of a system in equilibrium (where discharge is equal to recharge). Inversely, if the recharge rate is greater than that of discharge then the residence time of the system will be greater than that of a system in equilibrium.

Several methods have been developed in order to date groundwater resources in order to estimate the groundwater residence time, including physical modelling as well as chemical

analysis. However as the expected residence time of the groundwater in the Waiamakriri-Avon River system is less than one year (Taylor et al., 1989), methods used for 'young' groundwater (<60 years old) will only be presented. These methods predominantly rely on conservative chemical tracers such as stable isotopes or the radioactive decay of certain elements (Kazemi et al., 2006). The use of oxygen and hydrogen isotopes as conservative tracers is highly useful tool as they are the composition of water molecules. Radioactive elements are also useful but require very accurate measurements of low concentration elements that naturally occur within the system, and there is a degree of uncertainty as to where they may have been sourced or originated. Flow modelling using software programmes, such as MODFLOW, are also used to simulate groundwater flow based on input variables. This method has its limitations with results only being as good as the inputs, as well as variables which cannot be accounted for within the software itself such as irregularities (i.e. faults) within the flow medium.

Stable isotope analysis was chosen as the primary method used to constrain the residence time of the groundwater in the Waimakariri-Avon River system. The facilities available at the University of Canterbury enable accurate stable isotopic analyses to be conducted within the budget of this thesis. Sample sizes required for testing are small (2ml) and multiple samples can be carried out within a short period of time.

2.4 STABLE ISOTOPE ANALYSIS

2.4.1 STABLE ISOTOPE HYDROGEOLOGY

Certain periodic elements have varying atomic masses due to varying numbers of neutrons within their nucleus. These differently weighted atomic states, of the same element, are called isotopes. Isotopes can be stable, undergo no natural radioactive decay processes, or unstable (radioactive) and undergo radioactive decay, forming new isotopes or elements (Kazemi, et al., 2006). Certain stable isotopes of hydrogen, oxygen, carbon, nitrogen, and sulphur can be used to study hydrogeological processes that effect surface and groundwater. Radioactive isotopes can also be used to determine the age of older groundwater (Fetter, 2001).

2.4.2 WATER ISOTOPE ABUNDANCES

As mentioned previously, hydrogen and oxygen both have multiple stable forms of isotopes that can be used to study ground and surface water. As hydrogen and oxygen isotopes comprise water molecules they provide a built-in tracer for analysing water (Sharp, 2007). The most commonly used hydrogen isotopes that are used in water analysis are protium and deuterium. Both forms have a single one proton but deuterium also has a single neutron (Figure 2.9). The most commonly used oxygen isotopes in water analysis are oxygen-16 and oxygen-18 (Oxygen-18 has two more neutrons than oxygen-16). These are represented visually in Figure 2.9. Another stable oxygen isotope exists, oxygen-17, but is not as commonly used in isotopic water analysis.

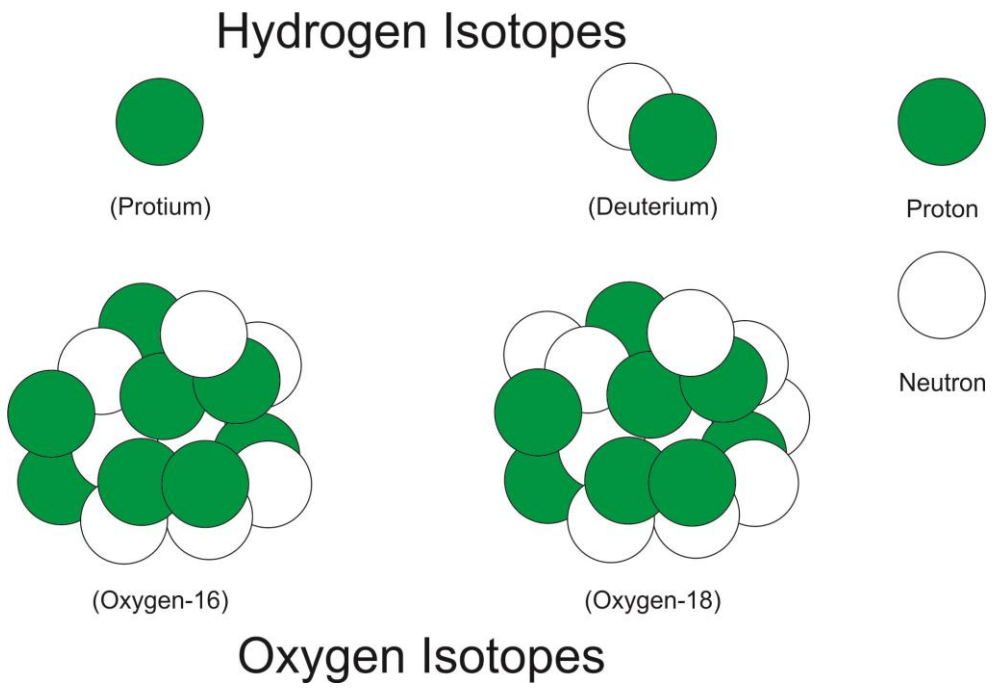


Figure 2.9: Schematic showing the different nucleuses of the differing isotopic states of hydrogen and oxygen commonly used in water isotope analysis.

The natural occurrence of each varying isotope can be measured and quantified, in terms of relative abundance, as a proportion to other isotopes of the same element. This enables water molecules (containing one oxygen isotope and two hydrogen isotopes) to form with varying isotopic combinations, known as isotopologues (Table 2.2).

Stable Isotope	Average Abundance (%)
Protium (H)	99.9844
Deuterium (D)	0.0156
Oxygen-16 (^{16}O)	99.7621
Oxygen-18(^{18}O)	0.2000
Isotopologue	**Average Abundance (%)**
$H_2{}^{16}O$	99.73098
$H_2{}^{18}O$	0.199978
$HD^{16}O$	0.031460
$HD^{18}O$	0.0000006
$D_2{}^{16}O$	0.00000002
$D_2{}^{18}O$	0.00000000005

Table 2.2: Relative abundances of stable isotopes commonly used in water analysis and isotopologues (modified from Sharp, 2007). Note percentages do not include the contributions of oxygen-17.

2.4.3 WATER ISOTOPE RATIOS AND STANDARDS

The varying masses between the two isotopic states results in separation into heavy or light fractions, also known as isotopic fractionation. Fractionation occurs naturally as a result of evaporation or heating (Fetter, 2001). As there are relatively large differences in atomic weight and abundance of oxygen and hydrogen isotopes, ratios between the various isotopic states of each element can be made. Using equation 2.6, the level of relative fractionation, δ, can be determined by the ratio, R, of the heavy isotope to the lighter isotope.

$$\delta\ (‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} x\ 1000 \qquad Eq.\ 2.6$$

where, R_{sample} is the ratio of the sample, and $R_{standard}$ is the ratio of a given standard (modified from Sharp, 2007).

The commonly used standard, in current isotopic studies, is the Vienna Standard Mean Ocean Water (V-SMOW). V-SMOW was obtained by distilling seawater, superseding the

previous standard of SMOW (Standard Mean Ocean Water), and has been an internationally accepted standard for almost half a century (Clark & Fritz, 1997). Therefore equation 2.6 can be rewritten with respect to ^{18}O and D (deuterium);

$$\delta^{18}O(‰) = \left[\frac{\left(^{18}O/^{16}O\right)_{sample}}{\left(^{18}O/^{16}O\right)_{V-SMOW}} - 1\right] x\ 1000 \qquad Eq.\ 2.7$$

$$\delta D(‰) = \left[\frac{(D/H)_{sample}}{(D/H)_{V-SMOW}} - 1\right] x\ 1000 \qquad Eq.\ 2.8$$

While V-SMOW is a useful reference point for comparing global water samples, ocean water is isotopically richer in ^{18}O and D than meteoric water due to preferential fractionation of lighter isotopes to heavier isotopes.

2.4.4 ISOTOPIC VARIATION

The fractionation of water isotopes, in particular ^{18}O, is primarily driven by heating processes (i.e. evaporation). Lighter isotopes are taken into vapour form more readily from sea water, leaving ^{18}O enriched water behind. While ^{18}O is also taken up in vapour, there is a greater abundance of ^{16}O present in the vapour mass. As the vapour cools, and condenses, the ^{18}O is preferentially taken into liquid form and precipitates out of the vapour mass. This leaves the vapour mass depleted in ^{18}O making it isotopically lighter with a higher proportion of ^{16}O (lower $\delta^{18}O$ values). As the vapour mass continues to condense, the subsequent precipitation will also be isotopically lighter, with respect to the previous precipitation, and the vapour mass will progressively become isotopically lighter (Figure 2.10); (Clark & Fritz, 1997).

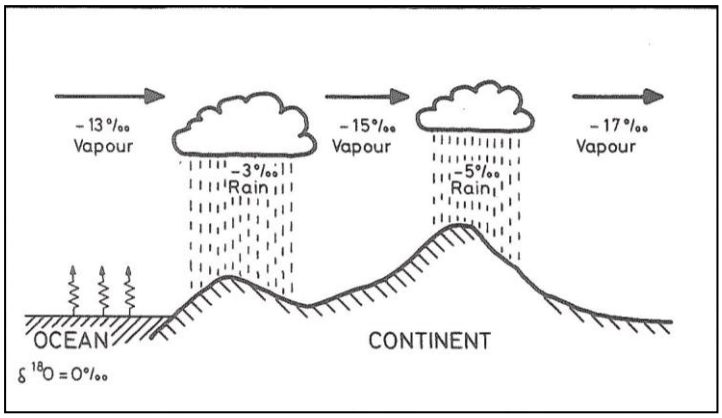


Figure 2.10:

Schematic showing fractionation of ^{18}O in the atmosphere (modified from Kenndall & McDonnell, 1998).

With this concept in mind, climate is therefore likely to have an effect on the ^{18}O uptake of vapour. As evaporation is a heat-driven process, warmer climates will have a higher rate of evaporation. With a higher rate of evaporation, a greater uptake of ^{18}O is likely to occur. The remaining ocean water also becomes enriched in ^{18}O as more ^{16}O is taken up in vapour form. It is noted in Clark & Fritz (1997) that cold regions are isotopically depleted compared to warmer regions, which were found to be isotopically enriched (Figure 2.11). This enrichment (or depletion) is the result of meteorological processes, mainly atmospheric movement of water vapour. As the enriched vapour rises into the atmosphere it is often subjected to subsequent movement by differing atmospheric pressures (wind). As a result of this, the precipitation of the vapour may occur far from the origin of evaporation and, after numerous cycles, alter the surface water enrichment of the ocean. This process of fractionation through precipitation is also known as Rayleigh fractionation, or distillation, and occurs over continental land masses (continental effect) as well as the by air mass movement poleward from the equator (latitude effect); (Kendall & McDonnell, 1998).

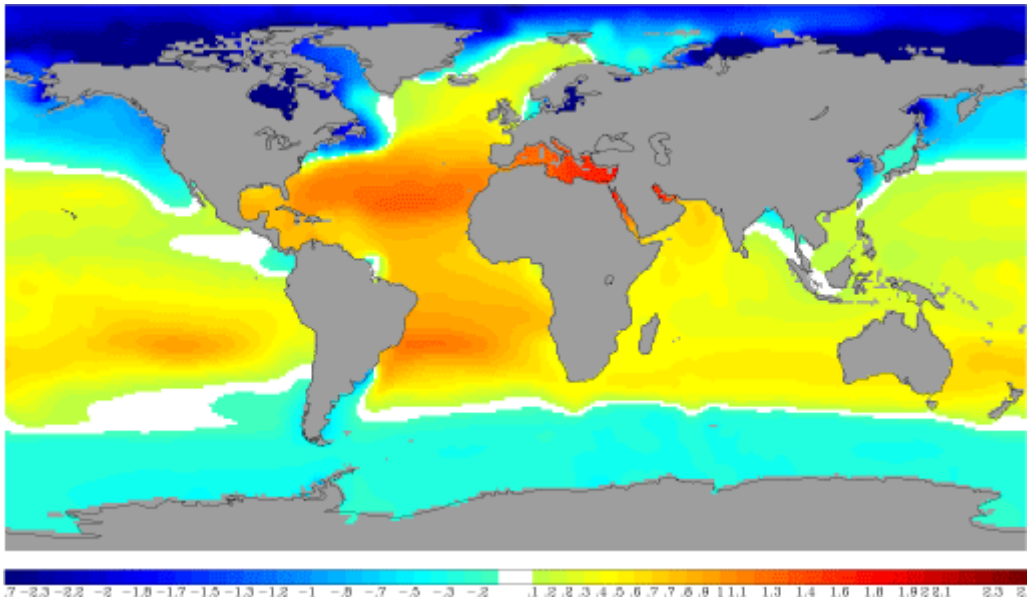


Figure 2.11: Surface δ ^{18}O values of global ocean water (Schimdt et al., 1999).

2.4.5 GLOBAL AND LOCAL METEORIC WATER LINES

$\delta^{18}O$ and δD values in fresh water are found to correlate on a global scale and led to the development of the global meteoric water line (GMWL) from numerous global freshwater samples (Figure 2.12); (Clark & Fritz, 1997).

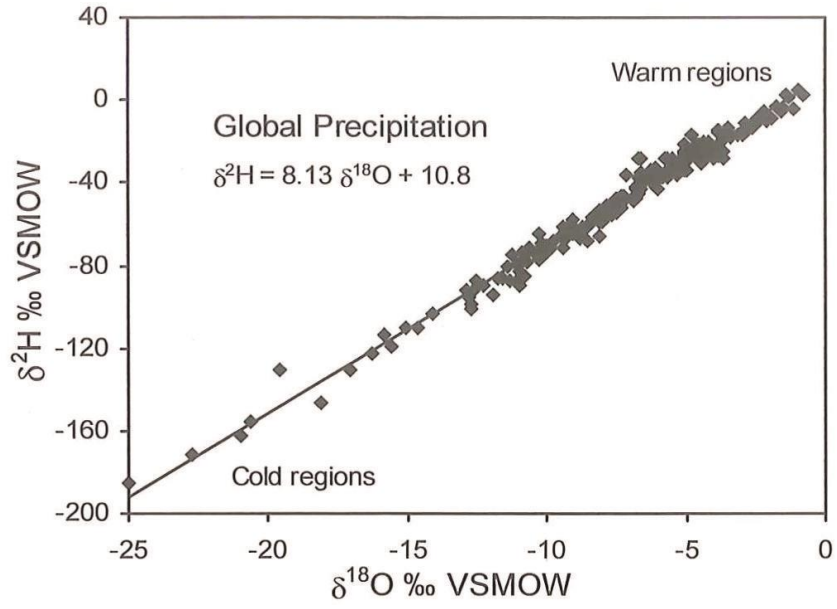


Figure 2.12:

The meteoric relationship of $\delta^{18}O$ and δD in precipitation (GMWL), and the variation between cold and warm regions (Clark & Fritz, 1997).

Water with an isotopic composition that plots along the GMWL is assumed to have originated from the atmosphere and to have been unaltered by other isotopic processes (Domenico & Schwartz, 1990). The GMWL is often characterised by the relationship;

$$\delta D = 8\,\delta^{18}O + 10 \quad \text{(Hoefs, 1987)} \qquad Eq.\ 2.9$$

Slight deviations from the GMWL occur as a result of climatic conditions (refer: Section 2.4.4) and can result in local meteoric water lines (LMWL), therefore geographic location can affect $\delta^{18}O$ and δD enrichment. LMWLs may not deviate strongly from the GMWL, but do give an indication of the long term meteoric trend of $\delta^{18}O$ and δD values for that region (Kendall & McDonnell, 1998).

2.4.6 APPLICATIONS FOR GROUND AND SURFACE WATER TRACKING

The use of the GMWL and the LMWL provide useful reference points for interpreting the origin of ground and surface water. Deviations from the LMWL indicate that the ground or surface water may originate from a different source or undergoing isotopic alteration as a result of water-rock interaction. In many cases water-rock interactions affect the $\delta^{18}O$ and δD values in such a way that the position of the data points can help identify the process responsible for the deviation (Figure 2.13); (Domenico & Schwartz, 1990).

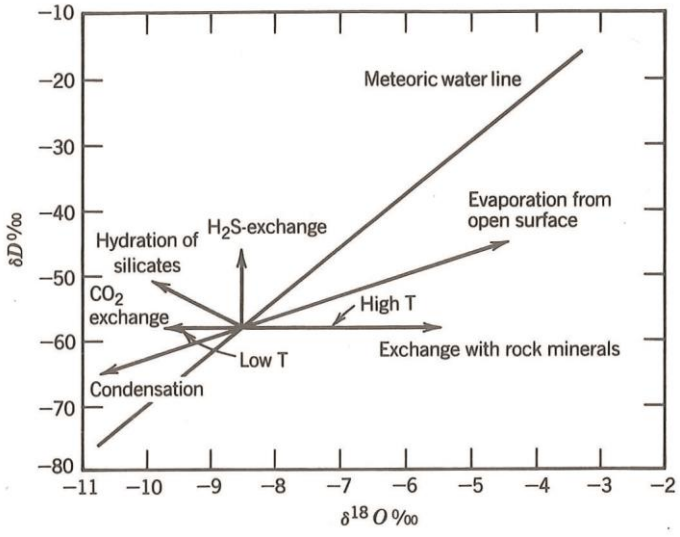


Figure 2.13:

Deviations in isotopic compositions away from the meteoric water line as a result of various processes (Domenico & Schwartz, 1990).

The local precipitation values of $\delta^{18}O$ and δD also provide important information as to the origin and major source of recharge for streams as well as groundwater. Fluctuations in isotopic concentrations may be attributed to seasonal variations, such as snow melt (which

is isotopically light as a result of Rayleigh fractionation, refer: Section 2.4.4), or storm events, which may result in a short term flux of isotopically variable precipitation, differing from the average $\delta^{18}O$ and δD precipitation values (Hoefs, 1987). These fluctuations can be useful in terms of characterising and measuring the hydrogeological processes that are occurring. Measuring the fluctuations in the ground and surface water systems can help to constrain, if not determine, the amount of water entering the system, the residence time of the system and the time taken for the water to enter the system through recharge processes (refer: Section 2.2.2).

2.5 ANIONIC ANALYSIS

2.5.1 IONS, CATIONS AND ANIONS

Atoms in their elemental state have no net charge, due to a balance of positively and negatively charged particles (protons and electrons); (Faure, 1986). Certain atoms react with others resulting in a loss or gain of an electron. This results in an overall net charge of the atom, as there is an imbalance of positively charged particles (protons) and negatively charged particles (electrons). As electrons are negatively charged particles, the gain of an electron results in the atom becomes overall negatively charged. Inversely, if an electron is lost the atom becomes positively charged. The resultant charged atom is called an ion. Ions with an overall negative charge are classified as anions, where positively charged ions are classified as cations (PSU, 2014). Cations and anions can bond together to form ionic compounds. Some of these compounds are able to dissolved and mobilised by water. Ions dissolved in water are deemed to exist in an aqueous state. These aqueous solutions are able to transport ions through water pathways and remain in aqueous state until they are removed from solution. This occurs by way of precipitation through evaporation, saturation or reacting to form a compound that is less soluble in water.

2.5.2 WATER CHEMISTRY

Ions occur in ground and surface waters in varying concentrations. This is highly dependent on the environment surrounding the water bodies. Natural processes, such as water interactions with geology and vegetation, can contribute to ion concentration changes, which may be reflected in surface and ground water chemistry and overall water quality

(Fetter, 1999; Appelo & Postma, 1993). Salt water mixing with fresh water bodies is often identified by an increase in salinity levels, predominantly chloride anions. Weathering of minerals also releases concentrations of ions into water bodies with highest concentrations observed at the source, or point of 'injection', into the water system (Fetter, 1999). Many natural processes (i.e. water-rock interaction) occur over long time scales. As a result, their chemical effects are well integrated into in the ground and surface water systems they impact.

Effects from anthropogenic (human-based) activities such as gas emissions, agriculture and waste disposal can also have a noticeable effect on the water chemistry and quality (Fetter, 1999). While some anthropogenic processes may have only been operating over a short time scale, certain activities can have long lasting effects altering water chemistry for days, months, or decades following cessation of the activity (Fetter, 1999). Leachate from fertilizers or improperly sealed landfills have detrimental effects on ground and surface water systems. Depending on duration of injection and solubility of the leachate, as well as the characteristics of the ground and surface waters (flow rate and direction), effects can be localised or wide spread. These can have adverse effects of human health if consumed in excessive doses, and once they enter the groundwater system, the effects can be long lasting and difficult, as well as costly, to remediate (Appelo & Postma, 1993; Fetter, 1999).

Determining the hydrogeological processes present in the area of study and understanding the effects and processes, natural or anthropogenic, that are resulting in a chemical change in ground and surface water is key to determining the source of the chemical alteration. Certain ions or ionic compounds are generally associated with anthropogenic processes, such as nitrate, but understanding the background (natural state) of the ground and surface water helps to determine the contribution of both natural and anthropogenic processes to the water chemistry and quality.

2.5.3 APPLICATIONS FOR GROUND AND SURFACE WATER TRACKING

By observing changes in ground and surface water chemistry it is possible to deduce the effects natural and anthropogenic processes are having on anion concentrations within the water. As the chemistry changes temporally, as well as spatially, it is also important to consider variations in both natural and anthropogenic influences as well with time and

space (Fetter, 1999). Changes in chemical concentrations are likely to be the result of water mixing from a different source, or ionic compounds dissolving into aqueous state (Appelo & Postma, 1993). By observing fluctuations in anion concentrations it is possible to determine various influences on the ground and surface water systems. The natural occurrences of the following anions were used as tracers, in conjunction with isotopes, to help identify surface and groundwater flow paths and influences.

Chloride (Cl^-): Chloride naturally occurs in ocean water in doses around 18980 mg/l (Stanford University, 2014). Concentrations in fresh water vary with proximity to the coast but are significantly lower in concentration to that of the ocean (<100 mg/l); (Fetter, 1999). Chloride is also taken into the atmosphere within evaporated sea water (Avery et al., 2001)

Nitrate (NO_3^-): Natural sources of nitrate are converted from nitrogen in the atmosphere by cyanobacteria in oceans and lakes as well as bacteria living on the roots of plants, such as legumes and lichen. Artificial sources of nitrate are predominantly sourced from fertilizers. Typical concentrations of nitrate in soils (non-fertilized) are around 4.5 mg/l (Fetter, 1999).

Sulfate (SO_4^{2-}): Sulfate is an oxidised state of sulphur. Sulphur is released by the weathering of minerals containing the element. Sulphur is also commonly used in the forms of fertilizers and pesticides (Fetter, 1999), as well as a component of sea water (Avery et al., 2001)

Nitrite (NO_2^-): Nitrite is very reactive and is almost instantly converted to nitrate, so normally very little nitrite is found in the environment (Fetter, 1999).

Fluoride (F^-): Fluoride naturally occurs in freshwater in concentrations <1 mg/l and is also used in toothpaste. Fluoride is sometimes added to municipal water supplies, but in concentrations less than <2 mg/l. High concentrations may be attributed to hydrofluoric acid contamination from industrial processes (Fetter, 1999).

Bromide (Br^-): Bromide occurs naturally in very small concentrations and is used as an organic compound in some industrial solvents and pesticides (Fetter, 1999). It is also naturally occurring in sea water at concentrations of around 65mg/l (Avery et al., 2001).

2.6 SUMMARY

Hydrogeological principles are fundamental in any ground or surface water analysis along with understanding the interactions between these two parts of the hydrologic cycle and with the atmospheric source. Fluctuations between these three hydrologic reservoirs is an important consideration when determining groundwater recharge rates. The properties of the materials (rock/soil), in which the groundwater is present, controls many variables associated with subsurface flow rates, such as the hydraulic conductivity and hydraulic gradient. The aquifer type and the interaction of ground and surface water, as well as other aquifer systems, emphasises the complexity of groundwater systems. It is therefore critical to understand the geology of an area in order to understand the factors controlling groundwater flow.

The use of water chemistry is a useful tool for ground and surface water tracking applications. Isotopic analysis of oxygen and hydrogen was the method chosen to constrain the residence time of the groundwater in the Waimakariri-Avon River system with the facilities readily available at the University of Canterbury. The factors governing and constraining the variations in isotopic values are well documented and understood. It is important to characterise the local precipitation and sources of recharge for ground and surface water bodies in the area of study in order to fully understand the effects that may be occurring within the subsurface. Anionic analysis of water also provides another useful tool for identifying potential sources of natural or anthropogenic processes. Concentrations of chloride, bromide, nitrate, sulfate, nitrite and fluoride anions were determined as they can be identified with probable sources. Understanding the baseline chemistry of a site or area is critical in order to determine significant variations in isotopic or anionic concentrations as well as determining the origins of such variations.

CHAPTER 3: STUDY AREA AND METHODOLOGY

3.1 INTRODUCTION

This chapter presents an overview of the hydrogeology beneath Christchurch and the surrounding area (Figure 3.1). Aspects of the known geology, ground and surface water interactions, and major recharge sources are presented from investigations undertaken in the past. A review of Christchurch's precipitation, ground and surface water chemistry was undertaken to determine baseline isotopic compositions and anionic concentrations. Having an understanding of the baseline concentrations of ground and surface waters, as well as in precipitation, allows deviations and fluctuations to be more clearly identified. It also enables the identification of contributors to the ground and surface waters and their origins. In order to constrain the residence time of the Waimakariri-Avon River system, precipitation and surface water samples were collected over 4.5 months, from March to July, 2014. Samples were collected during and after two large rainfall events in March, 2014, which had distinct isotopic signatures. Surface water sample sites were sampled once a week, with one site sampled daily. Precipitation samples were collected after each individual rainfall event. Samples were then analysed for their isotopic compositions and anionic concentrations. The methods used to carry out the investigation are presented with details of the sample sites, the quantity of samples collected and the methods used to analyse and process the collected samples.

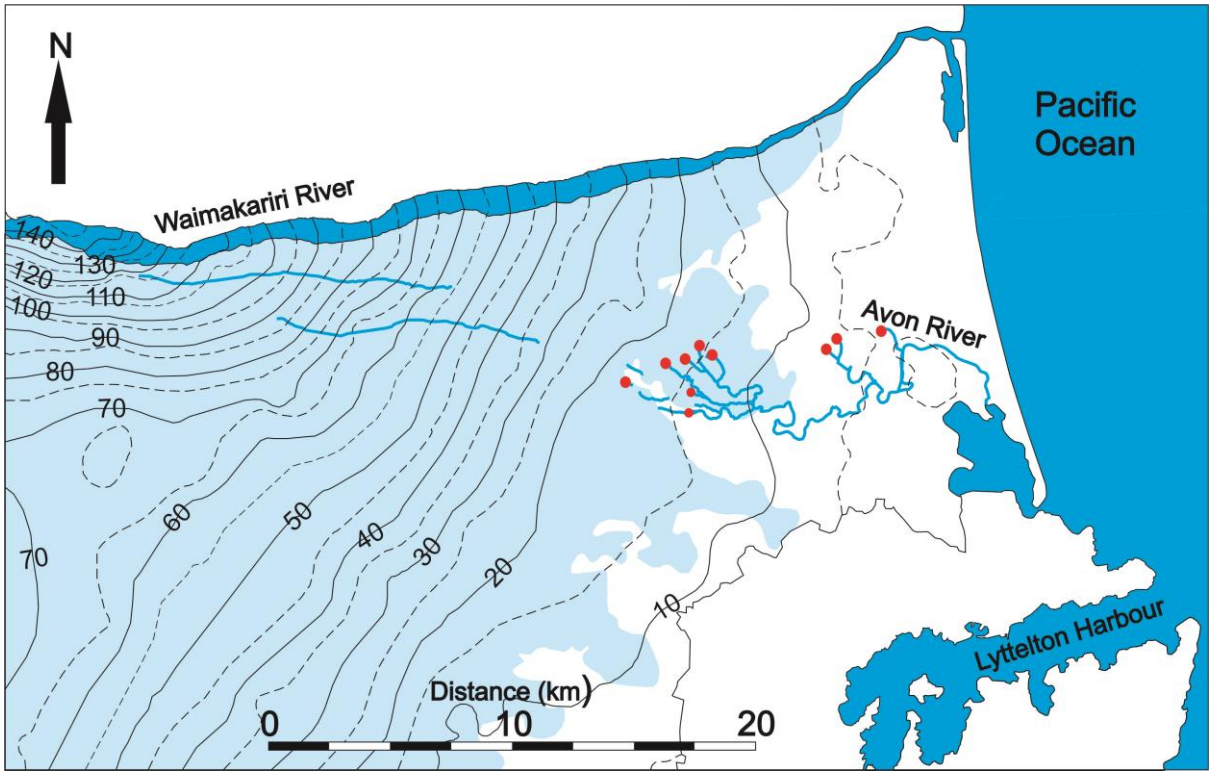


Figure 3.1: Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system. Contours indicate depth to the water table with groundwater flow in the direction perpendicular to contour lines. Blue lines indicate surface water flow paths. Red dots indicate known Avon River tributary springs.

3.2 HYDROGEOLOGY OF CHRISTCHURCH

3.2.1 GEOLOGY OF CHRISTCHURCH

Christchurch is situated mid-way along the coast of the Canterbury Plains, in the South Island of New Zealand. The plains are the result of overlapping alluvial fans derived mostly from glacial-fed rivers, originating in the Southern Alps. The relatively rapid uplift (~8mm/year) of the Southern Alps resulted in rapid erosion and deposition during the late Quaternary, inundating the Canterbury Plains with alluvial deposits. The well graded, fine to coarse alluvial gravels underlying the Canterbury Plains are of the order of 500 m thick (GEER, 2011) and consist primarily of greywacke, an argillitic metamorphosed sandstone composed largely of silica (Brown & Weeber, 1992). Towards the coast, these gravels are interbedded with coastal, estuarine, lagoonal and swamp deposits of gravel, sand, silt, peat and clay (Figure 3.2). These sediments also interfinger the gravel deposits near the coast,

accumulating during fluctuations in sea level, during glacial advance and retreat, and are typically thicker at the coast, progressively tapering as they extend inland (Figure 3.3); (ECan, 2002).

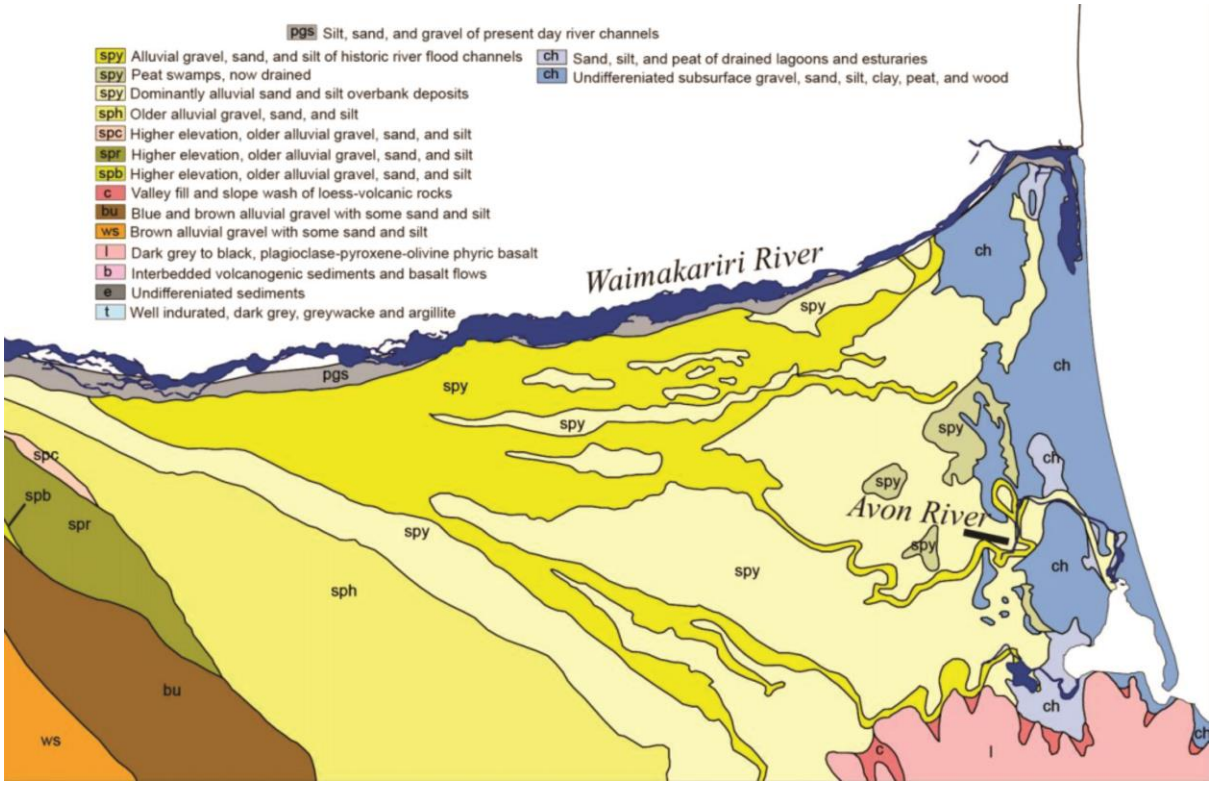


Figure 3.2: Surficial geology of the Christchurch area (Brown & Weeber, 1992).

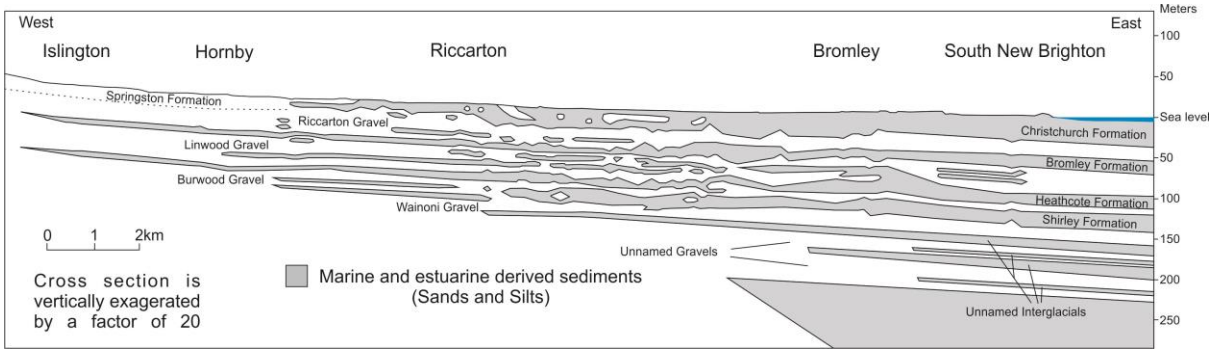


Figure 3.3: Stratigraphy of interfingered aquifer gravels and confining marine/estuarine sediments beneath Christchurch (modified from Brown & Weeber, 1992).

Banks Peninsula formed as the result of a mafic volcanic complex around 11-6 Ma and is now considered to be extinct (Brown & Weeber, 1992). The eroded basaltic landform is largely overlain by loess, a glacially derived wind-blown deposit, which ranges in thickness of between 1-20+ m (GEER, 2011).

On September 4th, 2010 and February 22nd, 2011 Christchurch was subjected to two large (7.1Mw and 6.2Mw respectively), separate earthquake events and numerous aftershocks (GNS, 2013). The February, 2011 earthquake resulted in noticeable effects on the subsurface material within Christchurch, in particular, liquefaction of the marine sediments in the eastern part of Christchurch. The western part of the city was less affected by liquefaction due to a deeper water table and the absence of fine grained marine sediments. While the effects of the earthquake appear to have had little effect on the western part of the city, effects such as consolidation and liquefaction of the subsurface material in the study area may have occurred. This is difficult to identify in order to determine whether any change has occurred when no visible signs are present at the surface. Changes to the unconfined aquifer's material properties, such as porosity and permeability, along the known subsurface flow paths identified by White (2009) and Callander (2005) could have altered the preferential flow path of the subsurface flow. Also to consider is the potential effect of damaged subsurface infrastructure (stormwater and sewerage drains), which may be leaking into the groundwater system beneath the city.

3.2.2 HYDROLOGY OF CHRISTCHURCH

Christchurch has many spring-fed rivers flowing through urban areas, but the two main surface water bodies of focus in this study are the Waimakariri River and the Avon River. As previously mentioned (refer: Section 2.3.3), surface and groundwater flows from higher potentiometric levels to lower potentiometric levels. Figure 3.4 shows the groundwater contours of the upper unconfined (water table) aquifer beneath the Christchurch area. The higher potentiometric contours originate from the Waimakariri River and radiate south and eastward, indicating that the Waimakariri River is the main source of groundwater in the Christchurch area. It has been suggested by Taylor et al. (1989) that Waimakariri-derived shallow groundwater will take no longer than 1 year to reach the boundary of the confined zone 10 km away, implying an average hydraulic conductivity value of 3.17×10^{-4} m/s or 27.4 m/day. The Avon River is a spring-fed system with base flows controlled by discharge from the underlying gravel aquifers and historic river channels which have since been buried.

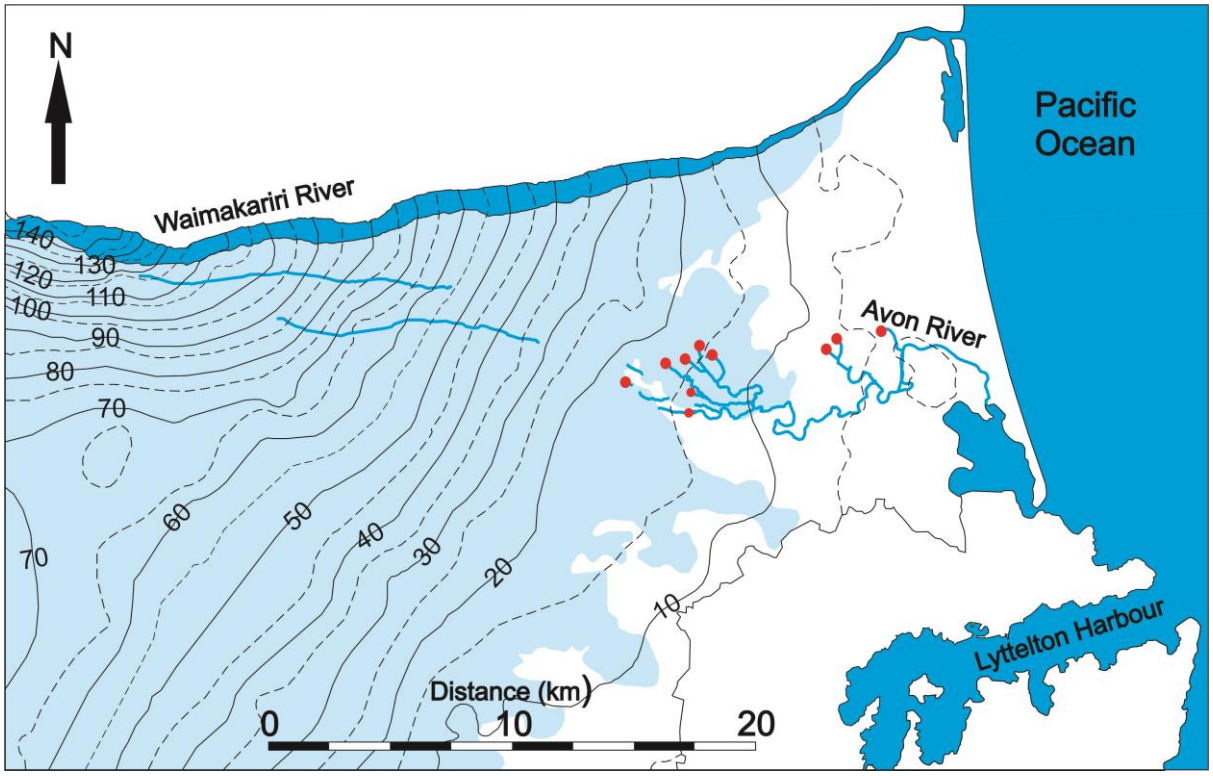


Figure 3.4: Potentiometric contours of the upper unconfined aquifer (water table) beneath and west of Christchurch. Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system. Red dots indicate known spring sites of Avon River tributaries.

Several studies have been conducted on the Christchurch aquifer system as it is the source of all freshwater for the city (White, 2009). The recharge of groundwater is mainly sourced from lateral subsurface flow and percolation of Waimakariri River water, with contributions from precipitation, into the underlying Quaternary sediments (GNS, 2008; White, 2009; White et al., 2012). The gravels beneath Christchurch act as the aquifers, with high permeability, effective porosity and hydraulic conductivity. Groundwater movement within the upper unconfined aquifer varies as localised channels of more permeable gravels permit higher rates of flow (GNS, 2008).

The interfingered marine and estuarine sediments, that act as a confining layer, restrict flow between the upper unconfined aquifer and the underlying gravel aquifers and induces a confining pressure on the confined gravel aquifers. The recharge rate and residence time of the aquifers increases with depth due to the restriction of flow between aquifers. This study focuses on the interactions of the upper unconfined aquifer between the Waimakariri and Avon Rivers and the rivers themselves.

3.3 GEOCHEMICAL COMPOSITION OF CHRISTCHURCH WATER

3.3.1 PRECIPITATION WATERS

The isotopic signature of rainfall events in the Christchurch area varies with the origin of the vapour mass. A study by Blackstock (2011) collected 65 samples from precipitation events in Christchurch. The findings of his study determined $\delta^{18}O$ and δD values to vary between 0‰ to -14 ‰ (V-SMOW) and 0 ‰ to -110 ‰ (V-SMOW), respectively. Mean values of Blackstock's (2011) study also deduced, through back-trajectory analysis, that the source of Christchurch's precipitation originates in the Southern and Tropical Pacific Oceans as well as in the Tasman Sea. The study also identified tropical cyclones as having very distinct isotopic signatures that lie well outside the normal range of locally derived precipitation events. Blackstock (2011) suggests a tropical cyclone event could be used as a groundwater tracer if its isotopic signature varies significantly from that of the locally derived precipitation and isotopic composition of the local ground and surface waters.

The anionic composition of rainfall is very dilute with very low anionic concentrations. Any significant anion concentrations of fluoride, bromide, nitrate, nitrite or sulfate are likely the result of anthropogenic or biogenic factors which are captured during fall out. Due to the proximal location of the ocean, concentrations of chloride may be attributed to sea spray (Avery et al., 2001).

3.3.2 SURFACE WATERS

Isotopic signatures of surface waters are expected to reflect those of the precipitation events that recharge them (Hoefs, 1987). With regard to the Waimakariri River, isotopic studies by Taylor et al. (1989), Blackstock (2011), and Cronin (2012) produced values of between -7.7‰ to -10.6‰ (V-SMOW) for $\delta^{18}O$ and -54.9‰ to -69.3‰(V-SMOW) for δD, the variance attributed to seasonal variations. The Avon River is expected to show a similar isotopic signature to that of the Waimakariri River, but the influence of precipitation may cause variable deviations.

The chemical composition of surface waters in Canterbury is well monitored by Environment Canterbury (ECan) and there is a known issue of river pollution within the Canterbury area (ECan, 2010). Cronin's (2012) study analysed water samples taken from the Waimakariri and

Avon Rivers, and anion concentrations are expected to be in the range of values attained from that study (Table 3.1).

Anion	Waimakariri River	Avon River
Chloride (Cl^-)	0.73-3.78 mg/l	0.73-3167.21 mg/l
Nitrate (NO_3^-)	0.45-0.63 mg/l	0.63-38.78 mg/l
Sulfate (SO_4^{2-})	2.87-4.39 mg/l	0.31-101.83 mg/l
Nitrite (NO_2^-)	BDL	0.01-1.99 mg/l
Fluoride (F^-)	0.26-0.36 µg/l	0.03-2.20 µg/l
Bromide (Br^-)	BDL	0.01-34.59 mg/l

Table 3.1: Summary table of anion concentrations obtained by Cronin's (2012) study (BDL=Below Detection Level).

Causes for variation in Cronin's (2012) samples collected from the Waimakariri River are attributed to seasonal variation and dilution or enrichment from rainfall events. Variation in the samples collected from the Avon River samples is attributed to influences of the proximity of some sites to the Avon River mouth, reflecting tidal influences, as well as contributions from sewerage and fertilizers.

3.3.3 UNCONFINED (WATER TABLE) AQUIFER WATER

The water present in the underlying unconfined gravel aquifer is expected to chemically reflect that of the Waimakariri River (as it is the major source of recharge) and the surface waters (which are dominantly fed by springs whose water originates from the underlying aquifers); (ECan, 2002). The gravels consisting of greywacke are relatively inert, so any water-rock interaction with the gravels is considered to be negligible. The marine sediments may have an influence on chloride levels, where interaction with groundwater occurs, but it is unknown to what extent. Where sea water intrusion or interaction between the confining layer and the groundwater occurs, the composition of the water is expected to reflect anionic ratios similar to that of sea water and may be used to identify the presence of sea water. Table 3.2 gives the mean anionic composition of sea water and ratio comparison to chloride.

Anion	Concentration (mg/l)	Ratio to Sea Water Chloride Concentration
Chloride (Cl^-)	18980	1.0
Nitrate (NO_3^-)	0.7	3.69×10^{-5}
Sulfate (SO_4^{2-})	2700	0.14
Nitrite (NO_2^-)	0.05	2.63×10^{-6}
Fluoride (F^-)	1.0	5.27×10^{-5}
Bromide (Br^-)	65	3.42×10^{-3}

Table 3.2: Mean anion concentrations in sea water (Stanford University, 2014; Avery et al., 2001).

3.4 HYDROGEOLOGICAL SYNTHESIS

The hydrogeology of the Christchurch area is complex, with a system of 'stacked' gravel aquifers. The dominant recharge source of the groundwater is the Waimakariri River to the northwest of the city, with a minor contribution attributed to localised rainfall. Recharge of the aquifers occurs as a result of water infiltration and percolation. The groundwater flow within the unconfined (water table) aquifer radiates south and eastward, from the Waimakariri River, through the subsurface along preferential flow paths, governed in part by past flow channels. The interfingering marine sediments act as a confining layer which induces confining pressures within the confined aquifers. In the presence of these pressures, and 'holes' in the confining layer, springs form supplying the base flow to many of the rivers and streams within the city area, including the Avon River. The chemical composition of the ground and surface waters is expected to closely reflect that of the Waimakariri River water, with any variations attributed to rainwater mixing, anthropogenic influences and interaction with the confining marine sediment layer.

In order to constrain the residence time of the groundwater in the Waimakariri-Avon River system, isotopically distinct rainfall events were targeted in order to provide a natural isotopic tracer to be used within the groundwater system. Table 3.3 summarises the expected range of isotopic values of precipitation, surface and aquifer waters.

Water Source	$\delta^{18}O$	δD
Meteoric Water	0‰ to -14.00‰	0‰ to -110.00‰
Waimakariri, Avon, Aquifer Water	-7.70‰ to -10.60‰	-54.90‰ to -69.30‰

Table 3.3: Summary of expected isotopic values for Christchurch water sources (Taylor et al., 1989; Blackstock, 2011; Cronin, 2012).

With the occurrence of large rainfall events in Christchurch being seasonal, few and isotopically distinct from 'normal' precipitation events, targeting such an event would introduce a significant volume of water into the Waimakariri-Avon River system with the potential of being an isotopic tracer. Reliance on such a tracer required sufficient precipitation to alter the chemistry of the surface waters of the Waimakariri River itself for a sufficient period of time in order to allow enough of the chemically altered water to enter the system. Two separate, large rainfall events were used to track the groundwater in the Waimakariri-Avon River system: a 1-in-100 year tropical low system that occurred between March 4th and 5th, 2014 and an ex-tropical cyclone (Lusi) which occurred between March 16th and 17th, 2014. The close spacing of the two storm events was thought to have provided a large volume of water capable of being integrated into the groundwater system, providing a distinct marker to be tracked along the flow path of the Waimakariri-Avon River groundwater system. While no anionic tracers were used to track the water, in the event of high rainfall events dilution is likely to occur within the system. Potentially this effect may also be tracked.

3.5 SITE SELECTION AND SAMPLE COLLECTION

3.5.1 SITE SELECTION

The surficial geology identifies potential preferential flow paths of groundwater in the form of past flow channels, and the potentiometric surface map indicates groundwater flow in the direction of the Avon River along these flow paths, originating from the Waimakariri River. As there is an abundance of publically accessible sites where spring or surface water can be collected, sites chosen were near or at spring locations, as well as potentiometrically down gradient of one another (Figure 3.5). Doing so enabled access to sampling sites to be unrestricted and reliable as well as providing a series of locations in which the isotopic

tracer could be tracked through the Waimakariri-Avon River system. Borehole water table sampling would have been preferable, but was not used over concerns of cost, private site access, sampling difficulty and time.

The chosen surface water samples were collected from: the Waimakariri River (WK) at the end of Haul Road, separate agricultural water raceways (MN & MS) along Chattertons Road, Avonhead Park (AP), the Okeover Stream at the University of Canterbury (UC), the Avon River (AR) at Hagley Park and a flowing artesian well at Lake Victoria (LV) at Hagley Park.

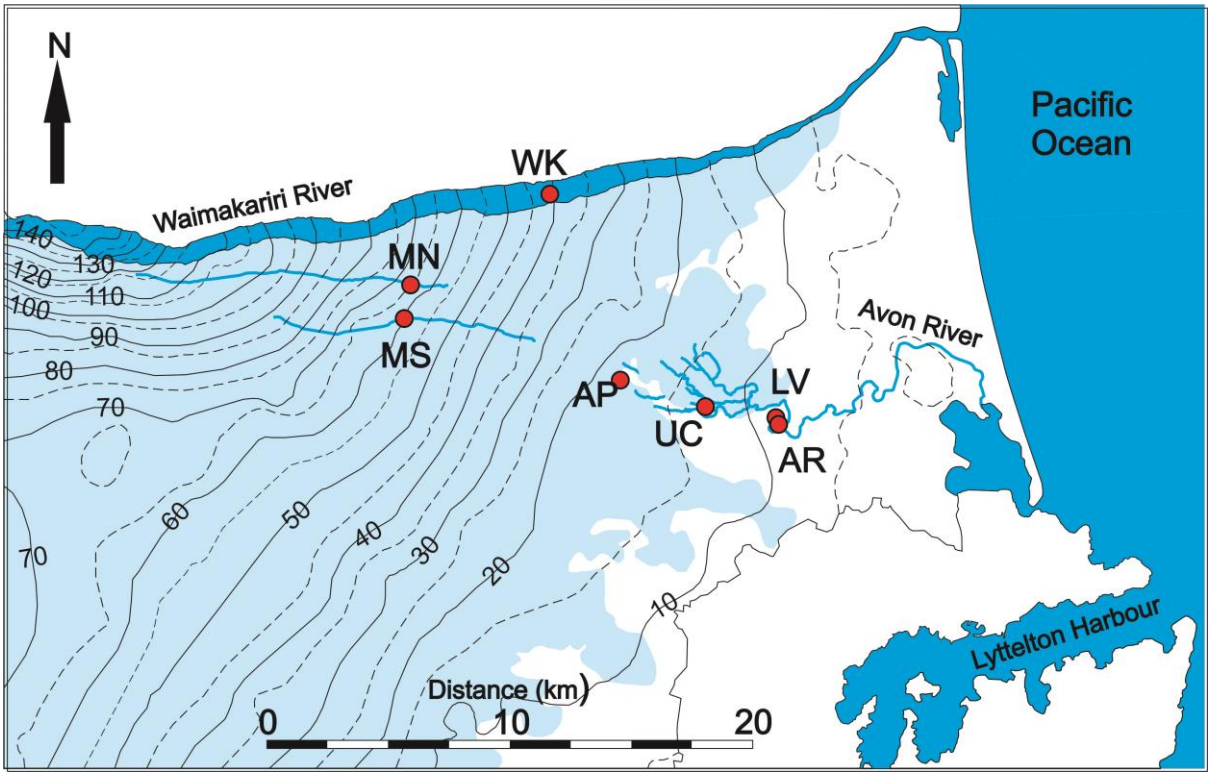


Figure 3.5: Study area and sampling locations of surface water samples that were collected. Rainwater samples were collected at the UC site location. Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system. Contours indicate depth to the water table with groundwater flow in the direction perpendicular to contour lines.

3.5.2 SURFACE WATER SAMPLING

Sampling was undertaken at regular intervals for an extended period of time in order to provide long term data, enabling identification of deviations from baseline conditions. A total of 7 sites were used to collect samples between March and August, 2014. Sites WK, MN, MS, AP, LV and AR were sampled weekly with site UC sampled daily. A total of 273

surface water samples were collected. Table 3.4 provides a summary of the number of samples collected at each of the sites.

Sample Site	Site Code	Number of Samples Collected
Waimakariri River	**WK**	**24**
Northern Raceway	**MN**	**26**
Southern Raceway	**MS**	**26**
Avonhead Park	**AP**	**24**
University of Canterbury	**UC**	**121**
Lake Victoria	**LV**	**26**
Avon River	**AR**	**26**
Total		**273**

Table 3.4: Summary of samples collected from each surface water sample site.

Samples were collected using a 60 ml syringe. The syringe was flushed a minimum of 3 times with water from the sample site prior to the sample being taken. When possible, the water was then filtered directly into a 50 ml plastic vial through a 0.45 µm PTFE filter. Where a filter was not available the sample was collected in the 50 ml vial and filtered in a laboratory at a later date. Vials were sterile prior to sample collection, with any contamination believed to be negligible. Samples were labelled with a site and sample code with the date and time of collection. Samples were then refrigerated until analysed for pH, isotopic compositions and anion concentrations.

3.5.3 RAINWATER SAMPLING

A total of 43 rainwater samples were collected from three sites (GEO, JH, EN) at the University of Canterbury over the sampling period (March-August, 2014); (Figure 3.6). GEO and JH samples were collected in rainwater collectors placed at ground level on the western side of the Von Haast building and on the roof of the Puaka-James Hight Library, respectively.

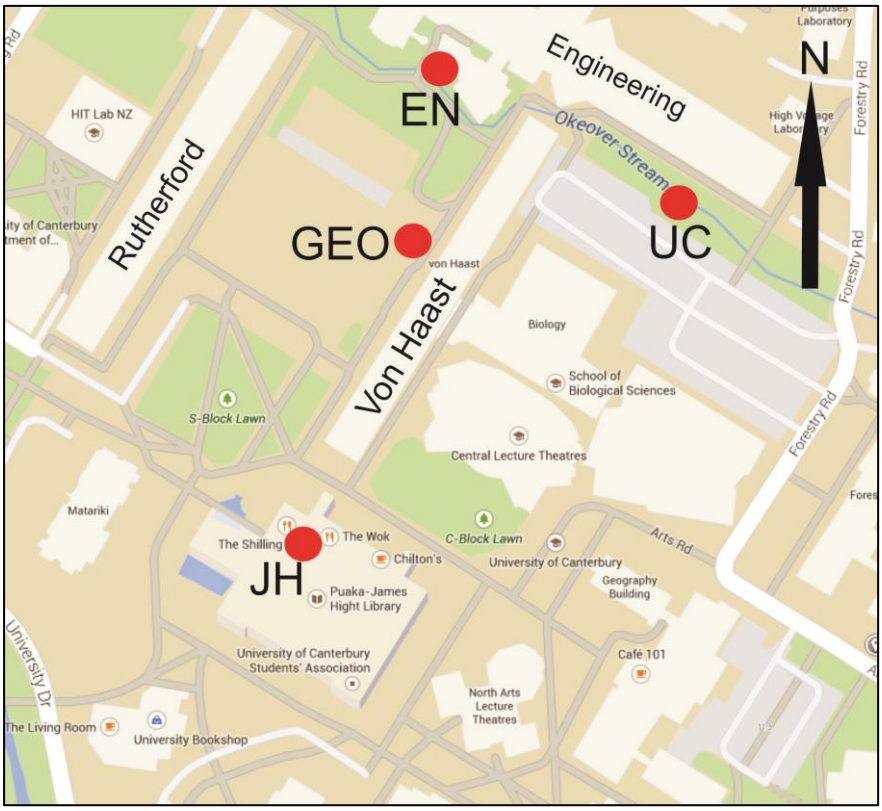


Figure 3.6: Locations of rainwater collection sites at the University of Canterbury as well as the location of surface water site UC.

The rain collectors comprised of a wide funnel that fed into a large flask (refer: Appendix I) that was sampled and emptied after, and at times during, significant rainfall events (flasks were only emptied during a rainfall event when the flask threatened to overflow). Flasks were interchanged, rinsed and oven dried between flask alternations. Samples were collected from site EN, a downpipe on the southern side of Engineering Block lecture theatre E8, during rainfall events (refer: Figure 3.6). Sampling methods are the same as previously mentioned (refer: Section 3.5.2). An additional 11 samples were collected by Travis Horton during the ex-tropical cyclone (Lusi) rainfall event (16-17th March, 2014). These samples were collected in 2 ml glass vials with a PTFE plastic cap. Daily rainfall volume data was collected from a local source in the Ilam area and can be sourced publically from Ilam weather (2014). Table 3.5 provides a summary of the number of samples collected at each of the sites.

Sample Site	Site Code	Number of Samples Collected
Von Haast Building	**GEO**	**20**
Puaka-James Hight Library	**JH**	**17**
Engineering Block	**EN**	**6**
Travis Horton		**11**
TOTAL		**54**

Table 3.5: Summary of samples collected from each rainwater sample site.

Vials were sterile prior to sample collection, with any contamination believed to be negligible. Samples were labelled with a site and sample code with the date and time of collection. Samples were then refrigerated until analysed for pH, isotopic compositions and anion concentrations.

3.5.4 RAINFALL RESPONSE SAMPLING

An additional 45 samples were collected in July 2014 over the course of a single rainfall event in order to provide a high sample frequency observation of the chemical response of surface water to rainfall events. Samples were collected between 4-11th July 2014 at 8 hour intervals from two tributaries of the Avon River and the Avon River itself; Okeover Stream (OK), Waimairi Stream (WM) and the Avon River (AV). Sampling was at the points of intersection with Clyde Rd, to the east of the University of Canterbury. Bulk samples were collected every 8 hours using a 10L bucket that was rinsed a minimum of 3 times with water from the site prior to the bulk sample being taken. Bulk samples were analysed for electrical conductivity in the bucket using a calibrated digital electrical conductivity meter in order to determine when the streams had returned to baseline conductivity readings, following rainfall dilution. Figure 3.7 shows the location of each of the sites in relation to one another and the surface water sample site UC. An additional gutter water sample was collected proximal to each of the sampling sites in order to identify potential influences of road runoff.

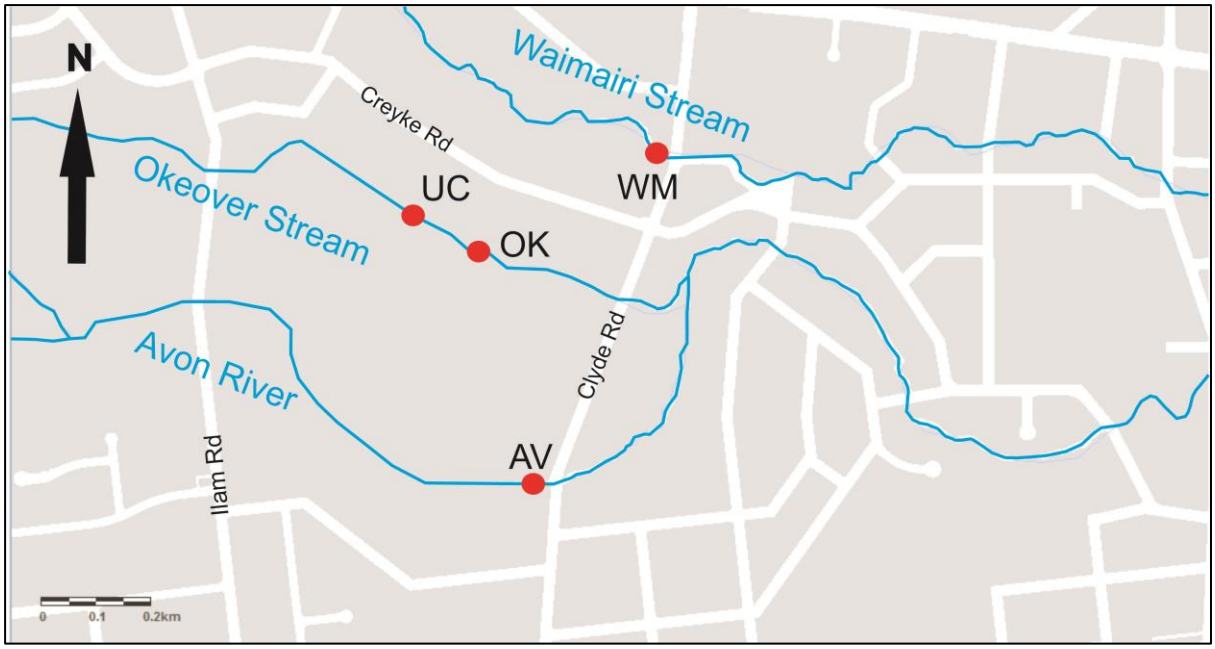


Figure 3.7: Sites used to collect 10L bucket samples with the University of Canterbury site (UC) as a reference.

A sample was then collected from the bulk sample in a 50 ml plastic vial following the same procedure as previously mentioned (refer: Section 3.5.2). Gutter water samples were also collected and filtered following the same procedure previously mentioned (refer: Section 3.5.2). Table 3.6 provides a summary of the number of samples collected at each of the sites.

Sample site	Number of samples collected
OK	15
WM	15
AV	15
Gutter samples	3
TOTAL	48

Table 3.6: Summary of samples collected from each stream site.

Vials were sterile prior to sample collection, with any contamination believed to be negligible. Samples were labelled with a site and sample code with the date and time of collection. Samples were then refrigerated until analysed for pH, isotopic compositions and anion concentrations.

3.6 SAMPLE PROCESSING AND ANALYSIS

3.6.1 PH PROCESSING AND ANALYSIS

The pH of each sample, with the exception of those collected by Travis Horton, was measured in a laboratory using a calibrated, digital pH meter (Thermo Orion 230). Samples were agitated prior to pH measurements. Full data set is presented in Appendix II. Between samples the pH meter probe was rinsed thoroughly with deionised water and dried with a paper towel. The calibration of the meter was tested prior to use, after being stored, using calibration liquids of pH =4 and pH = 7, where necessary recalibration of the meter was undertaken. While pH levels will be measured no analysis will be undertaken as they are not likely to aid in tracking the March, 2014 rainfall events.

3.6.2 ISOTOPIC PROCESSING AND ANALYSIS

Each sample was analysed at the University of Canterbury's Stable Isotope Facility (UCSIF), within the Geological Sciences Department. A Picarro L2120-i analyser was used in order to determine the isotopic composition of every sample taken with respect to δD and $\delta^{18}O$. Full data set is presented in Appendix II. The samples were prepared by using a 1 ml syringe to fill 2 ml glass vials with PTFE caps. The syringe was used to draw from the 50 ml sample vial and ejected into a waste beaker 3 times before being used to fill the 2 ml glass vial. This was repeated for each sample. The Picarro analyser simultaneously measures values for $\delta^{18}O$ and δD from optical spectra of specific stable isotopologues of water ($H_2{}^{16}O$, $H_2{}^{18}O$, and HDO) using a technique called Cavity Ring-Down Spectroscopy (CRDS). CRDS quantifies the optical absorption by measuring the rate of decay (the ring-down) of laser light in a cavity containing a gaseous sample (Picarro, 2010). Samples were calibrated against the world standard V-SMOW.

3.6.3 ANION PROCESSING AND ANALYSIS

Samples were processed in the University of Canterbury's 'SABRE' laboratory, within the Geological Sciences Department. Using a DIONEX ICS-2100 reagent free ion chromatograph, 213 samples were analysed for concentrations of chloride, nitrate, sulfate, nitrite, fluoride and bromide. Full data set is presented in Appendix II. The samples were prepared by pouring filtered samples from 50 ml vials into sterilised 6 ml plastic tubes which were

capped with a plastic cap. Calibration solutions were made for each cycle of samples that were analysed. The standard solutions made varied in concentrations between 0.05 and 20 mg/l and were made in bulk from a concentrate and diluted with deionised and UV treated water. The samples were then manually calibrated within the software program Chromeleon (c) Dionex 1996-2009 v7.1.0.898 to determine relative anion concentrations within each of the water samples being tested.

3.7 SUMMARY

The depositional geology of the Christchurch area has resulted in a series of interfingered fine to coarse gravels with marine, beach and swamp derived sediments, which have formed the basis of the Christchurch aquifer system. Past river and stream channels have provided an indicator as to prominent groundwater flow pathways which are likely to aid groundwater flow rates. The potentiometric surface of the area also supports the direction of the regional flow of the groundwater, radiating south and eastward from the Waimakariri River. Past studies have characterised many of the geochemical properties of the precipitation, surface and aquifer waters in the area, enabling a comparison to be made with data obtained from the samples collected. The two large precipitation events that have been used as tracers for this study are believed to have had a sufficient rainfall intensity and duration to provide a plausible tracer within the Waimakariri-Avon River system.

The sampling sites were chosen in order to capture the tracer as it moves through the Waimakariri-Avon River system and were suitable in both their location as well as their level of accessibility. The number of samples taken, at the stated frequency, has provided a sufficient amount of data, over a long period of time. The samples were collected in order to identify the isotopic tracer as it travels through the Waimakariri-Avon River system. The methods used to process and analyse the water samples are both accurate and reliable. The additional monitoring of rainfall influence has helped to discern any ‘false’ signals that may be caused by subsequent rainfall events as well as provide an insight into the time required for the surface waters to ‘recover’ geochemically, to baseline concentrations.

CHAPTER 4: RESULTS FROM ISOTOPIC AND ANION ANALYSIS

4.1 INTRODUCTION

The overarching aim of this thesis is to constrain the residence time of groundwater in the Waimakariri-Avon River system as it flows between the Waimakariri River and the Avon River. To achieve this 375 rainwater and surface water samples were collected between March and August, 2014 and all samples were analysed for their isotopic composition. Anion concentrations from 255 of the 375 water samples were also determined and the concentration summary for rainwater and each surface water site is presented below. Summaries of the geochemical composition of both rainwater and surface water are presented. Stable isotopic compositions are plotted relative to the GMWL as well as one another in order to identify relationships between different sites. Time series analysis of isotopic compositions and anion concentrations at each of the sample sites is also presented in an attempt to trace the water from the two large rainfall events that occurred in March, 2014 (see: Section 1.2). An attempt is also made to identify the spatial temporal characteristics of anion concentration response in surface waters as the result of precipitation events. Complete dataset is compiled in Appendix II.

4.2 ISOTOPIC COMPOSITION

This section presents the results of the isotopic analysis for each of the surface water sites that were collected on a weekly and daily basis as well as the rainwater samples.

Tables 4.1 and 4.2 summarise the δD and $\delta^{18}O$ values, respectively, determined at each of the surface water and rainwater collection sites (refer: Figures 3.5 & 3.6). Note Mean Rainwater includes values from the March, 2014 rainfall events used as the tracer.

δD (‰ V-SMOW)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
March, 2014 Events	**-12.62**	**-12.16**	**9.72**	**1.92 to -32.80**
Mean Rainwater	**-35.13**	**-30.52**	**27.55**	**1.92 to -112.31**
WK	**-60.65**	**-60.85**	**1.74**	**-55.80 to -63.52**
MN	**-60.36**	**-60.67**	**3.85**	**-48.11 to -70.08**
MS	**-60.21**	**-60.77**	**3.21**	**-50.22 to -67.83**
AP	**-58.04**	**-56.03**	**7.24**	**-33.47 to -73.38**
UC	**-57.34**	**-60.43**	**10.93**	**-7.41 to -72.55**
LV	**-59.45**	**-60.07**	**2.42**	**-47.95 to -60.95**
AR	**-58.72**	**-60.22**	**11.98**	**-22.23 to -88.64**

Table 4.1: Summary statistics for δD values obtained from surface water and rainwater samples (rounded to 2 decimal places).

$\delta^{18}O$ (‰ V-SMOW)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
March, 2014 Events	**-2.60**	**-2.63**	**1.06**	**-0.61 to -4.51**
Mean Rainwater	**-5.48**	**-4.79**	**3.29**	**-0.61 to -14.39**
WK	**-8.85**	**-8.84**	**0.22**	**-8.19 to -9.32**
MN	**-8.81**	**-8.85**	**0.48**	**-7.13 to -10.12**
MS	**-8.78**	**-8.82**	**0.40**	**-7.49to -9.93**
AP	**-8.08**	**-8.08**	**0.90**	**-6.16 to -10.22**
UC	**-8.24**	**-8.57**	**1.30**	**-2.13 to -10.03**
LV	**-8.59**	**-8.64**	**0.39**	**-6.83 to -9.02**
AR	**-8.53**	**-8.65**	**1.38**	**-4.32 to -12.22**

Table 4.2: Summary statistics for $\delta^{18}O$ values obtained from surface water and rainwater samples (rounded to 2 decimal places).

4.2.1 SAMPLE COMPARISON TO THE GLOBAL METEORIC WATER LINE

Figure 4.1 plots each of the surface and rainwater samples along with the Global Meteoric Water Line (GMWL). The majority of samples lie on, or close to, the GMWL indicating that the water has originated from a meteoric source, which is encouraging as it provides a baseline measure of the overall quality assurances associated with these analyses. Surprisingly, rainfall values vary widely with the majority of samples exhibiting δD and $\delta^{18}O$ values greater than -55.0 ‰ and -8.0 ‰ (V-SMOW), respectively. Surface water samples, in stark contrast are relatively consistent with values around -60.0 ‰ and -8.5 ‰ (V-SMOW) for δD and $\delta^{18}O$, respectively. The Avonhead Park (AP), University of Canterbury (UC) and Avon River (AR) sites show greater isotopic variation than the other surface water sites.

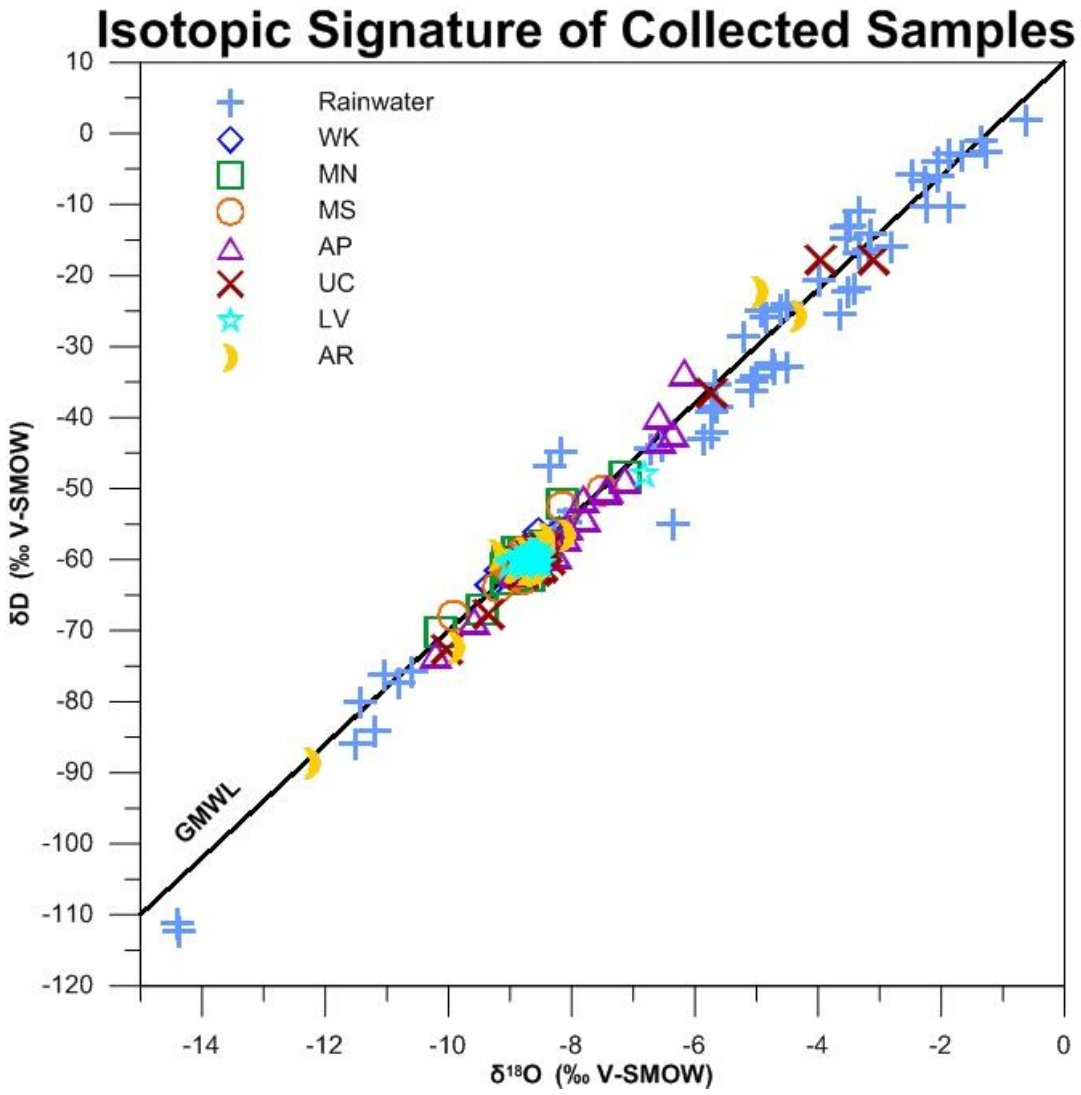


Figure 4.1: Samples compared to the GMWL with respect to their δD and $\delta^{18}O$ values.

4.2.2 ISOTOPIC VARIATION WITH RESPECT TO TIME AND RAINFALL

Figure 4.2 plots $\delta^{18}O$ values against time. Notably, the majority of sample sites have a baseline $\delta^{18}O$ value of between -8.5 ‰ to -9.0 ‰ (V-SMOW). Deviations from the baseline coincide with rainfall events (refer: Figure 4.2) as shifts in the direction of ^{18}O enrichment/depletion associated with the individual rainfall events. The Avonhead Park (AP), University of Canterbury (UC) and Avon River (AR) sites exhibit a clear deviation from the baseline $\delta^{18}O$ value and reflect rainwater $\delta^{18}O$ values following rainfall events. $\delta^{18}O$ values in rainfall samples are much more positive than local surface waters, predominantly falling between -4.0 ‰ to -6.0 ‰ (V-SMOW).

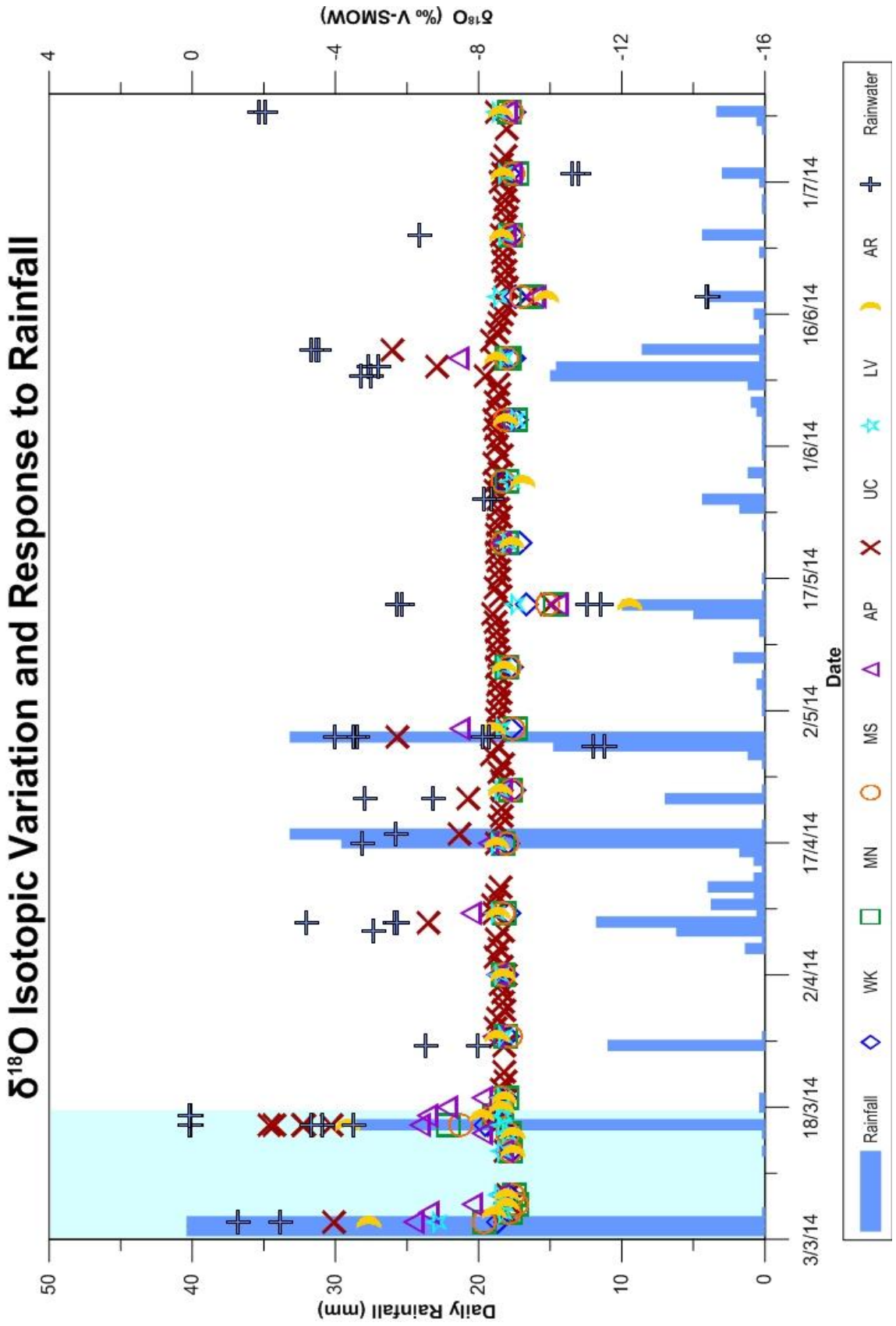


Figure 4.2: Sample $\delta^{18}O$ values versus time and rainfall. The blue bars correlate to daily rainfall and the data points are $\delta^{18}O$ values obtained from samples. The light blue section highlights the large rainfall events in March, 2014.

4.3 ANION CONCENTRATIONS

This section summarises and presents the results of the anion concentration analysis from all rainwater and surface water samples analysed. Each section reports the summary statistics for each anion analysed, the mean concentration at each site and changes in concentrations between sites with respect to time. The complete data set is presented in Appendix II. Rainwater values include those from the March, 2014 rainfall events.

4.3.1 CHLORIDE

Table 4.3 summarises the chloride concentrations determined from each of the surface water sites and rainwater samples.

Chloride Concentrations (mg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	8.52	6.84	7.79	0.53 to 29.02
WK	1.06	1.09	0.28	0.10 to 1.51
MN	1.28	1.17	0.59	0.83 to 3.82
MS	1.74	1.10	0.46	0.79 to 3.27
AP	3.05	2.13	1.50	0.93 to 11.75
UC	12.57	12.95	1.49	7.70 to 14.09
LV	9.04	9.07	0.14	8.50 to 9.25
AR	11.28	11.65	1.73	5.72to 13.32

Table 4.3: Summary statistics for chloride concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.3 plots the average chloride concentration measured at each of the sample sites versus distance from the Avon River mouth. The figure shows that the average chloride concentration in the samples increases with increased proximity to the mouth of the Avon River, as would be expected with minor amounts of salt-water mixing due to tidal fluctuations in estuary water levels. The average chloride concentration in rainwater was 1-3 mg/l less than those observed in surface water samples whose proximity to the Avon River mouth is closer than the sites used to collect rainwater samples.

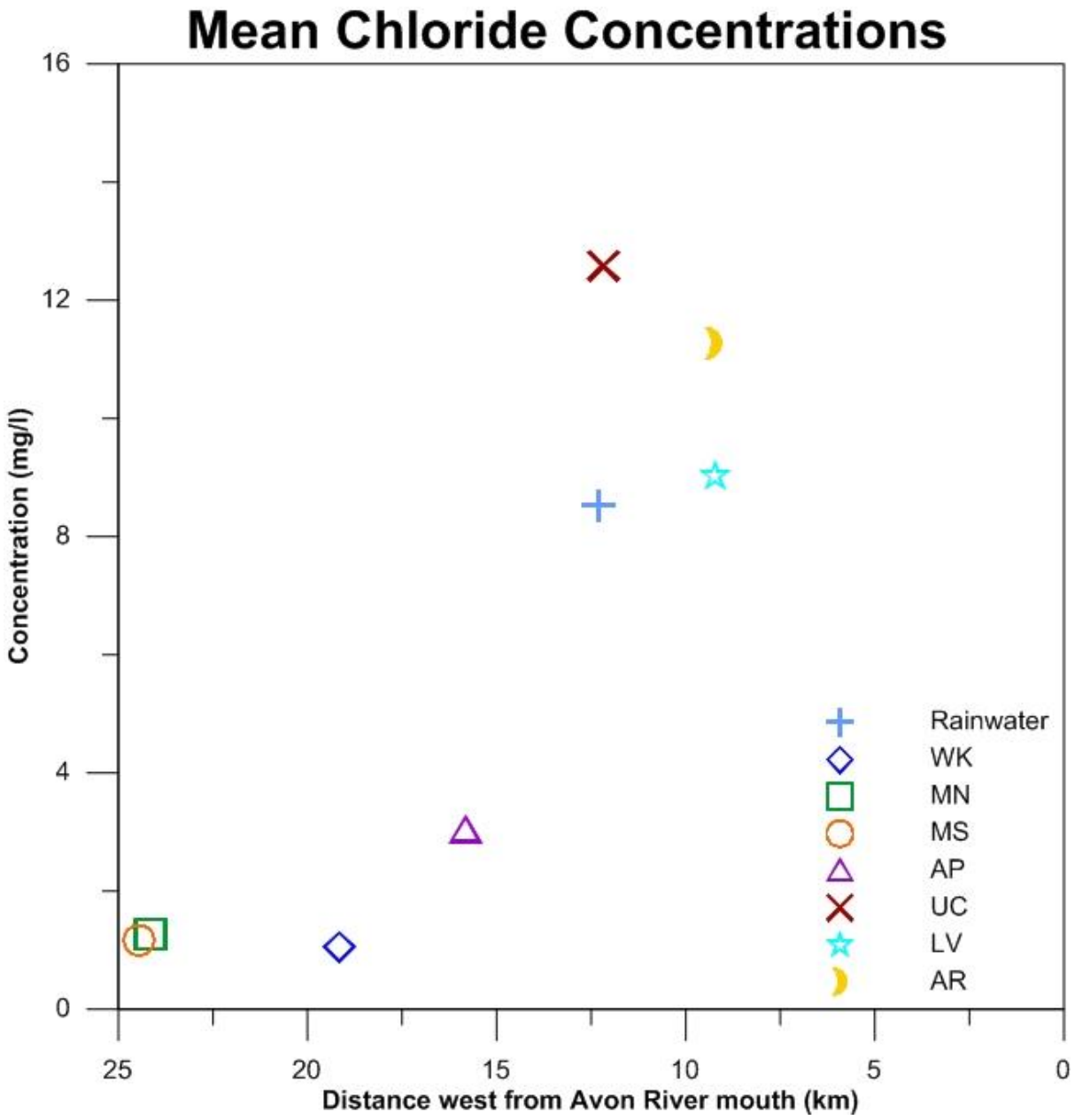


Figure 4.3: Mean chloride concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.4 plots the change in chloride concentrations between each site as a function of time. Each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Chloride concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

Deviations from baseline concentrations generally coincide with rainfall events. Sample sites WK, MN, MS and LV showed minimal response to rainfall events whereas sites AP, UC and AR demonstrated highly variable responses to rainfall events. Sample site WK, MN, MS, AP and LV all showed positive responses to rainfall indicating anion enrichment, whereas sites UC and AR showed negative responses to rainfall, indicating dilution. There are no distinguishable changes in chloride concentrations that can be traced through each of the sites in an attempt to trace groundwater derived from the large rainfall events in March, 2014.

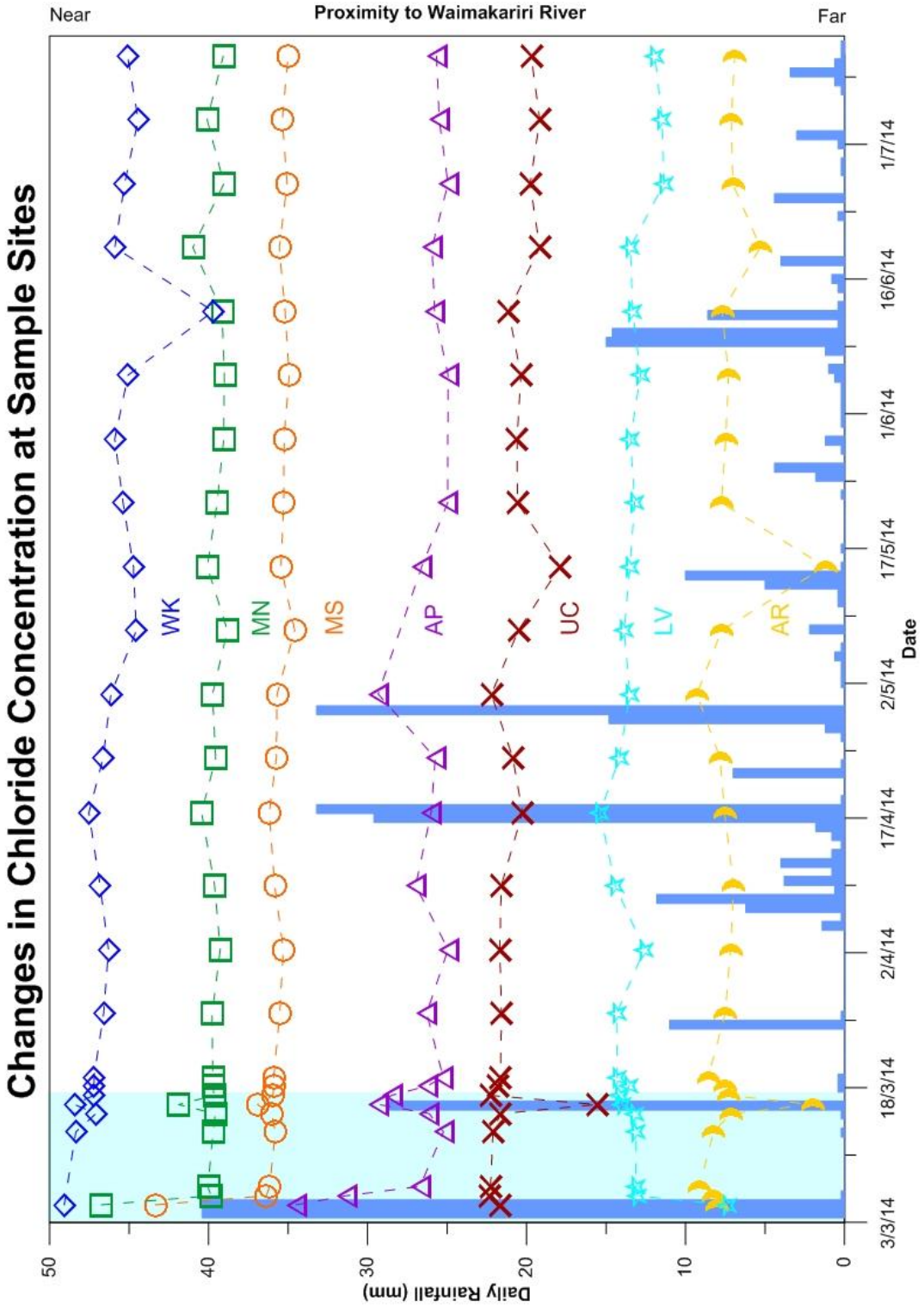


Figure 4.4: Chloride concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.3.2 NITRATE

Table 4.4 summarises the nitrate concentrations determined from each of the surface water sites and rainwater samples.

Nitrate Concentrations (mg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	1.08	0.56	1.16	0.01 to 3.85
WK	0.39	0.41	0.09	0.23 to 0.53
MN	0.13	0.09	0.12	0 to 0.39
MS	0.14	0.09	0.13	0 to 0.37
AP	0.43	0.07	0.50	0 to 3.65
UC	13.16	13.81	3.25	3.37 to 16.05
LV	10.30	10.60	1.61	2.63 to 10.99
AR	8.59	9.41	2.17	2.52 to 10.38

Table 4.4: Summary statistics for nitrate concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.5 plots the average nitrate concentration measured at each of the sites versus distance from the Avon River mouth. The figure shows that the average nitrate concentration in the samples increases with increased proximity to the mouth of the Avon River. The average nitrate concentration in rainwater is 7 mg/l less than those observed in surface water samples whose proximity to the Avon River mouth is closer than the sites used to collect rainwater.

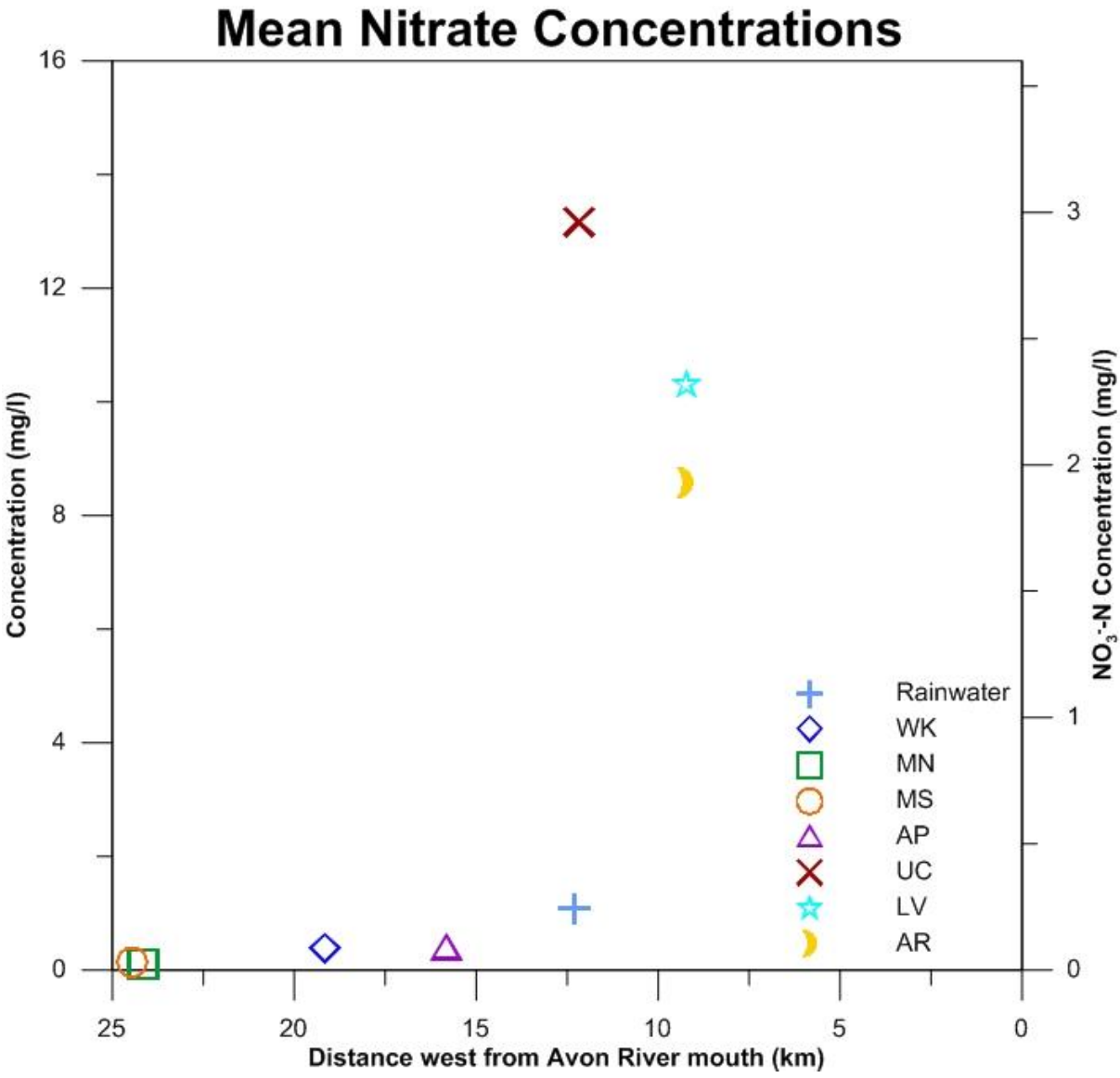


Figure 4.5: Mean nitrate concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.6 plots the change in nitrate concentration between each site as a function if time. As with chloride, each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Nitrate concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

As was the case with chloride, departures from baseline levels generally coincide with rainfall events. Sample sites WK, MN, MS and AP showed minimal response to rainfall events whereas sites UC, LV and AR demonstrated variable responses to rainfall events.

Sites WK, MN, MS, AP and LV all showed positive responses to rainfall indicating anion enrichment whereas UC and AR showed negative responses to rainfall indicating dilution. There are no distinguishable changes in nitrate concentrations that can be traced through each of the sites in an attempt to trace groundwater derived from the large rainfall events in March, 2014.

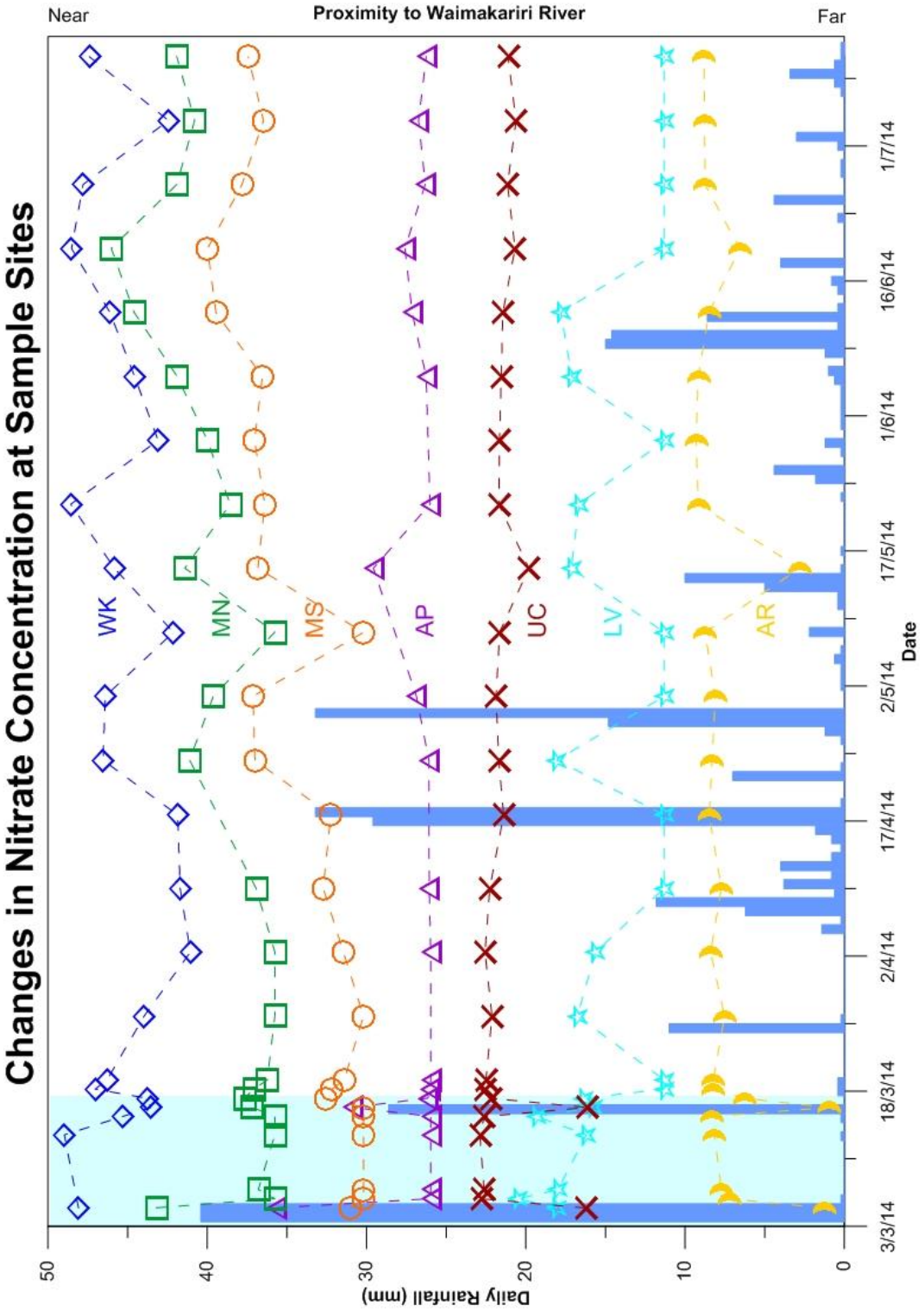


Figure 4.6: Nitrate concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.3.3 SULFATE

Table 4.5 summarises the sulfate concentrations determined from each of the surface water sites and rainwater samples.

Sulfate Concentrations (mg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	2.80	1.74	2.26	0.28 to 8.29
WK	4.66	4.60	0.66	3.46 to 5.49
MN	4.68	4.71	0.69	3.36 to 6.62
MS	4.53	4.54	0.81	2.23 to 5.66
AP	4.40	4.48	0.69	2.75 to 5.52
UC	10.85	11.37	1.93	4.59 to 12.95
LV	11.29	11.46	0.87	7.16 to 11.73
AR	10.96	11.36	2.27	4.35 to 13.82

Table 4.5: Summary statistics for sulfate concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.7 plots the average sulfate concentration measured at each of the sites versus distance from the Avon River mouth. The figure shows that average sulfate concentration in samples increases with increased proximity to the mouth of the Avon River by a factor of almost 3. The average sulfate concentration in rainwater was 2-8 mg/l less than all surface water sites suggesting meteoric water is only a partial source of sulfate anions. Surface water samples collected whose proximity to the Avon River mouth is closer than the sites used to collect rainwater showed the highest sulfate concentrations.

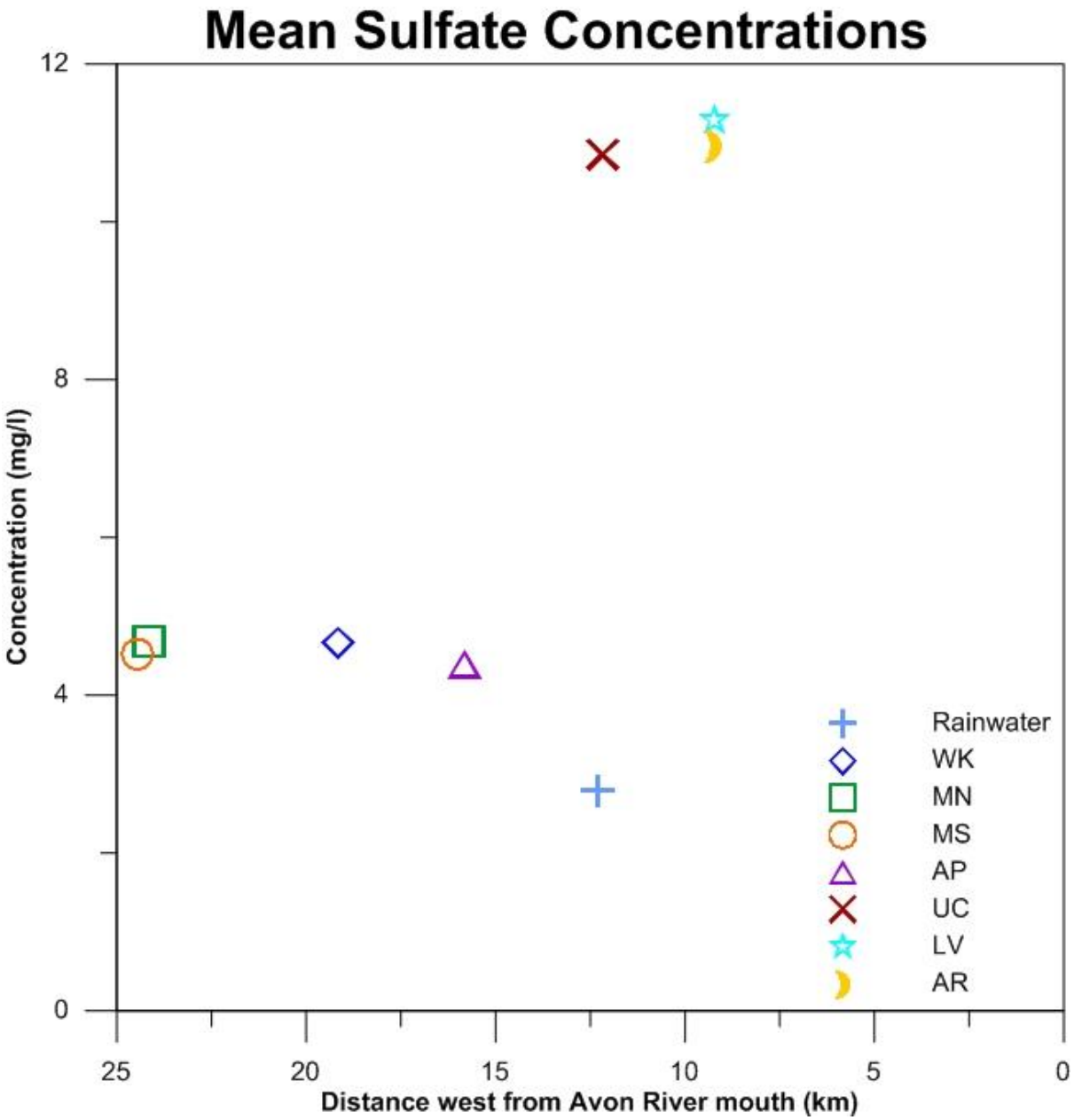


Figure 4.7: Mean sulfate concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.8 plots the change in sulfate concentrations between each site as a function of time. As with chloride and nitrate, each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Sulfate concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

Deviations from baseline levels appear to coincide with rainfall events, however sample sites WK, MN, MS and AP appear to decrease in baseline concentration following the sample collected on the 17th of April, the cause of which is unclear. Sample sites UC and AR demonstrated variable responses to rainfall events. LV shows no response to rainfall events with the exception of the sample collected on March 5th, 2014. There are no distinguishable changes in sulfate concentrations that can be traced through each of the sites in an attempt to trace groundwater derived from the two large rainfall events in March, 2014.

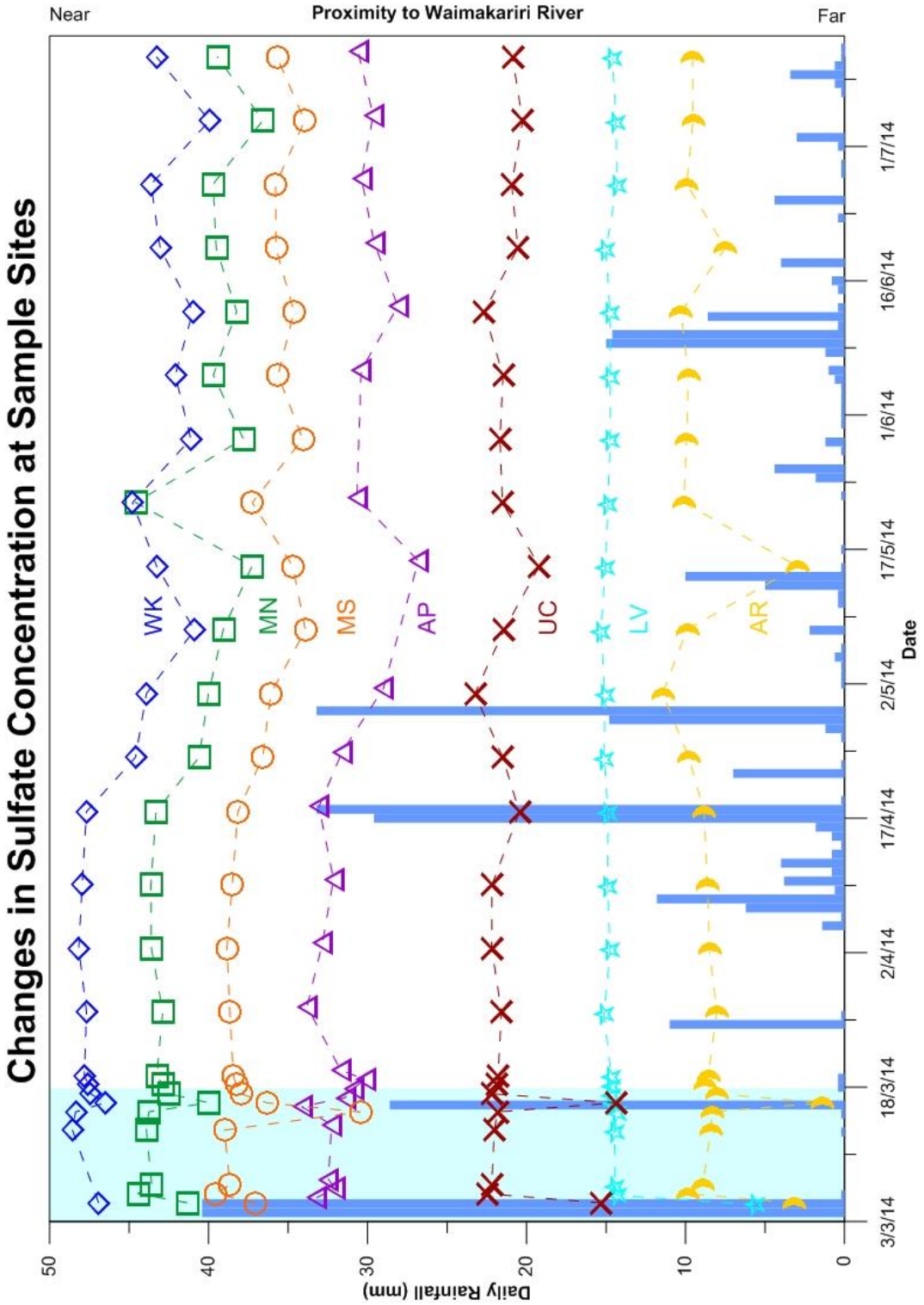


Figure 4.8: Sulfate concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.3.4 NITRITE

Table 4.6 summarises the nitrite concentrations determined from each of the surface water sites and rainwater samples.

Nitrite Concentrations (µg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	0.28	0.24	0.30	0 to 1.08
WK	0.03	0	0.10	0 to 0.44
MN	<0.01	0	0	0 to 0.10
MS	0.01	0	0	0 to 0.13
AP	0.02	0	0.10	0 to 0.21
UC	0.04	0	0.10	0 to 0.47
LV	0.04	0	0.10	0 to 0.24
AR	0.11	0.01	0.20	0 to 0.90

Table 4.6: Summary statistics for nitrite concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.9 plots the average nitrite concentration measured at each of the sites versus distance from the Avon River mouth. The figure shows that the average nitrite concentration in samples increases with increased proximity to the mouth of the Avon River. The average nitrite concentration in rainwater was significantly greater than those observed at surface water sample sites, indicating meteoric water as the primary source.

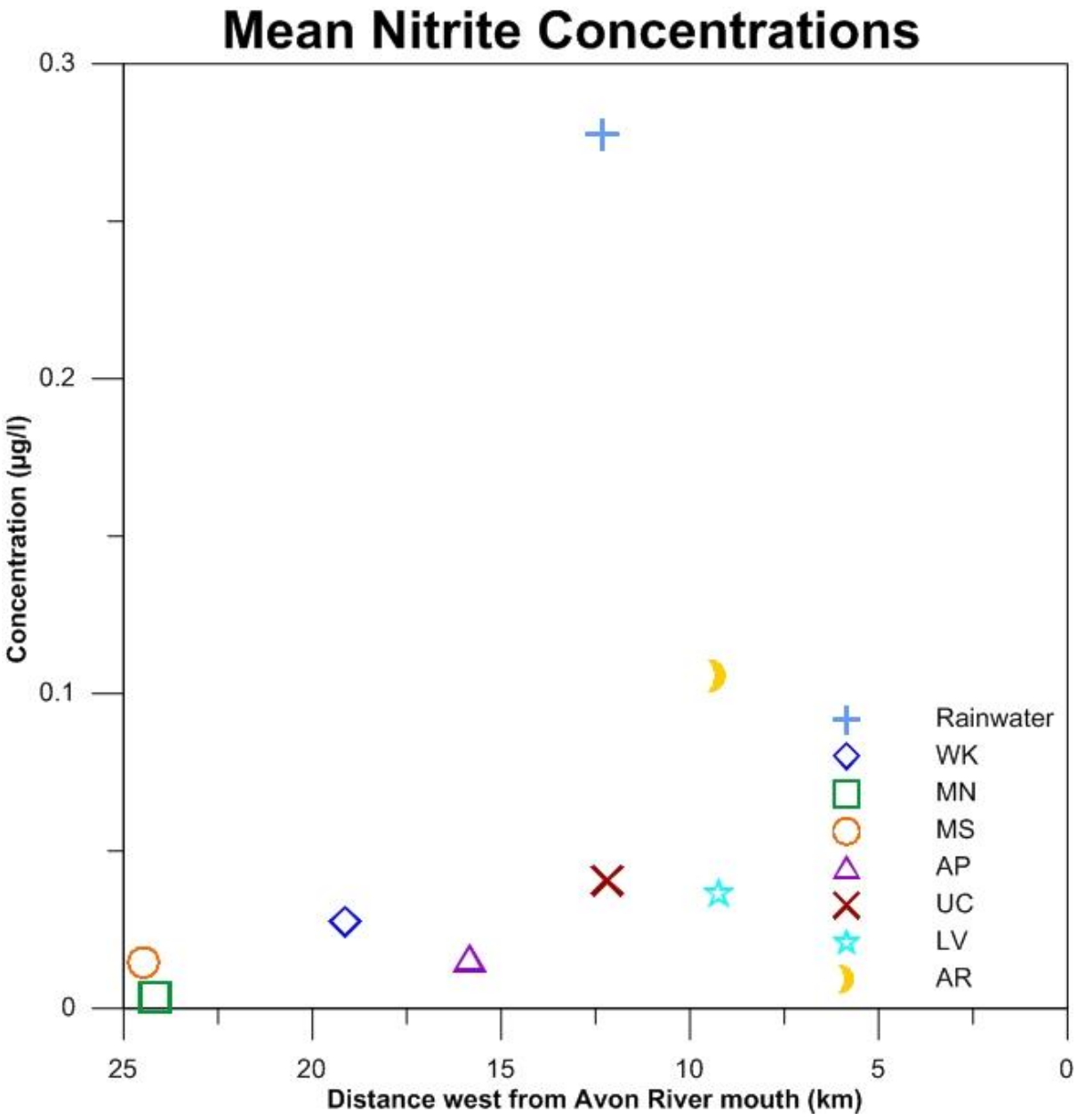


Figure 4.9: Mean nitrite concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.10 plots the change in nitrite concentration between each site as a function of time. As with previous anions, each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Nitrite concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

Deviations from baseline levels generally coincide with rainfall events but the response is variable. All sites have a baseline concentration of 0 µg/l, therefore any deviations are indicative of nitrite enrichment. There are no distinguishable changes in nitrite concentrations that can be traced through each of the sites in an attempt to trace groundwater derived from the two large rainfall events in March, 2014.

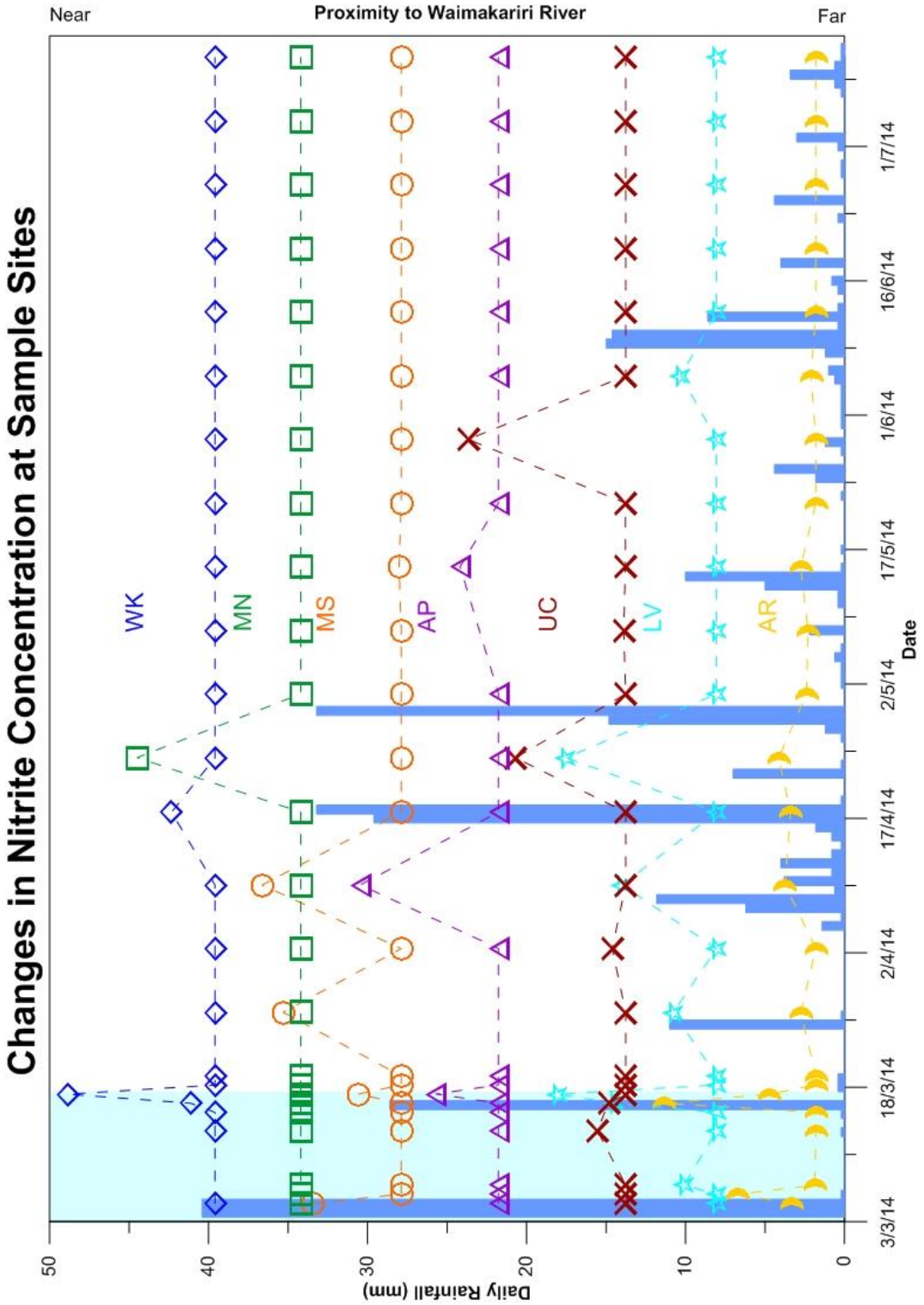


Figure 4.10: Nitrite concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.3.5 FLUORIDE

Table 4.7 summarises the fluoride concentrations determined from each of the surface water sites and rainwater samples.

Fluoride Concentrations (mg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	0.08	0.01	0.12	0 to 0.53
WK	0.04	0.04	0.01	0.02 to 0.05
MN	0.05	0.05	0.02	0.02 to 0.13
MS	0.04	0.05	0.01	0.02 to 0.06
AP	0.04	0.04	0.01	0.02 to 0.06
UC	0.03	0.03	0.02	0.02 to 0.10
LV	0.05	0.05	0.01	0.03 to 0.07
AR	0.04	0.04	0.01	0.02 to 0.05

Table 4.7: Summary statistics for fluoride concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.11 plots the average fluoride concentration measured at each of the sites versus distance from the Avon River mouth. The figure shows that fluoride concentrations in samples decreases with increased proximity to the mouth of the Avon River. The average fluoride concentration in rainwater was higher than those observed at surface water sample sites suggesting a meteoric source.

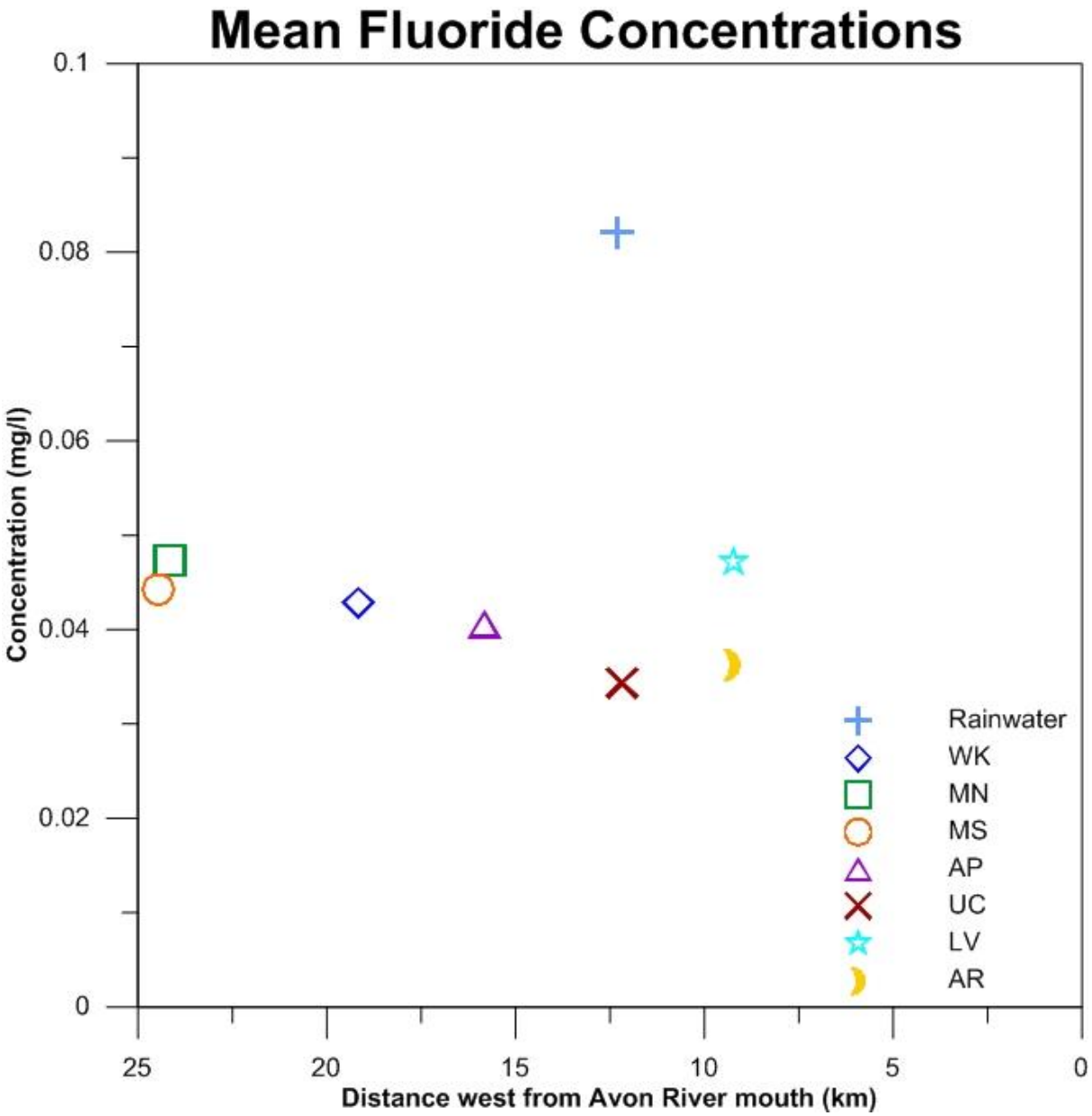


Figure 4.11: Mean fluoride concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.12 plots the change in fluoride concentration between each site as a function of time. As with previous anions, each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Fluoride concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

Deviations from baseline levels generally coincide with rainfall events with variable responses. There is no distinguishable change in fluoride concentrations that can be traced through each of the sites in an attempt to trace groundwater derived from the two large rainfall events in March, 2014.

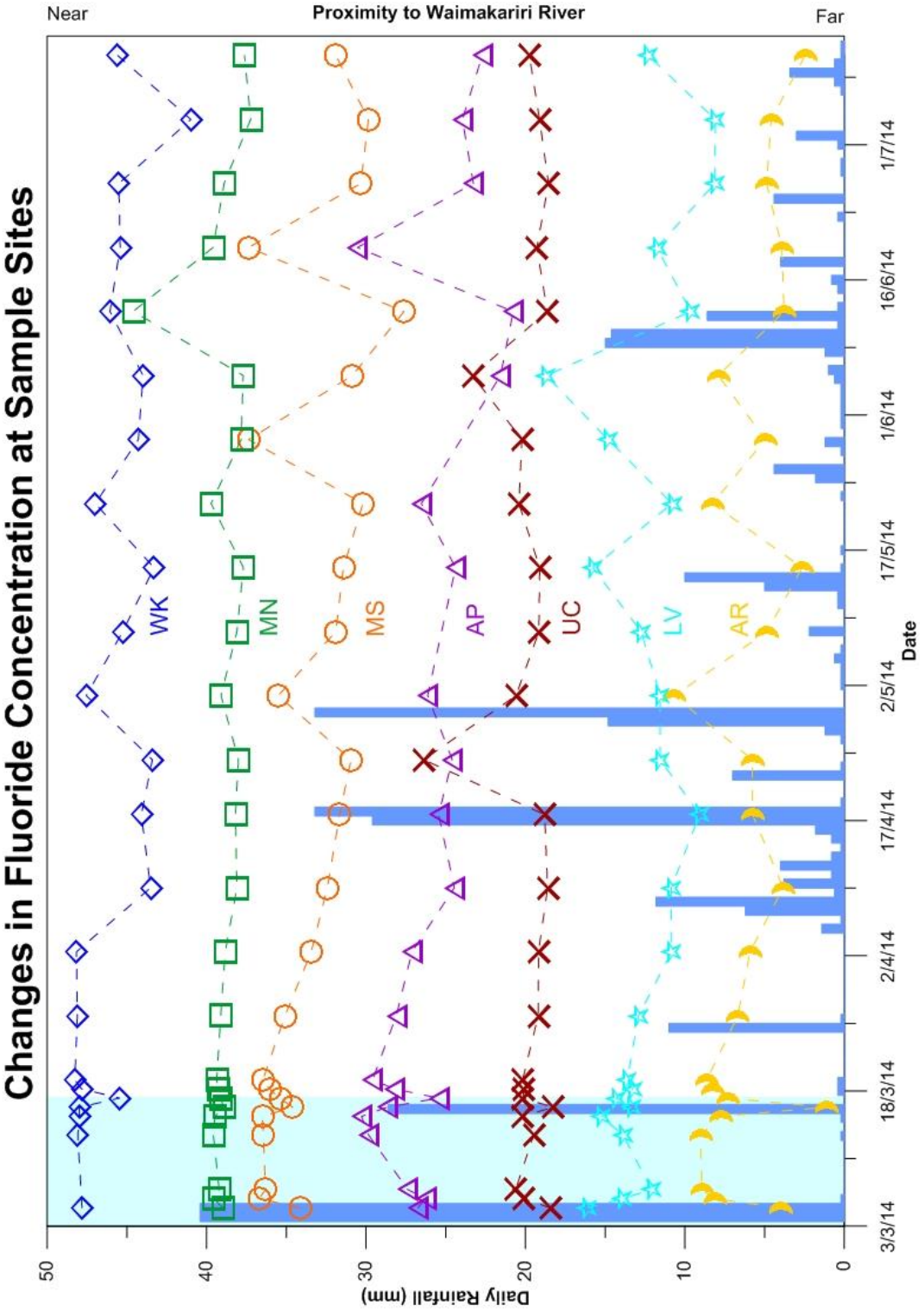


Figure 4.12: Fluoride concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.3.6 BROMIDE

Table 4.8 summarises the bromide concentrations determined from each of the surface water sites and rainwater samples.

Bromide Concentrations (µg/l)				
Sample Site	**Mean**	**Median**	**Standard Deviation**	**Range**
Rainwater	0.03	0	0.10	0 to 0.28
WK	Below detection levels			
MN	Below detection levels			
MS	Below detection levels			
AP	0.01	0	0	0 to 0.20
UC	0.10	0	0.10	0 to 0.29
LV	0.13	0.17	0.10	0 to 0.35
AR	0.11	0.11	0.10	0 to 0.38

Table 4.8: Summary statistics for bromide concentrations obtained from surface water and rainwater samples (rounded to 2 decimal places).

Figure 4.13 plots the average bromide concentration measured at each of the sites versus distance from the Avon River mouth. The figure shows that bromide concentrations in samples increases with increased proximity to the mouth of the Avon River. The average bromide concentration in rainwater was significantly less than those observed at surface water sample sites whose proximity to the Avon River mouth was closer than that of the rainwater collection sites.

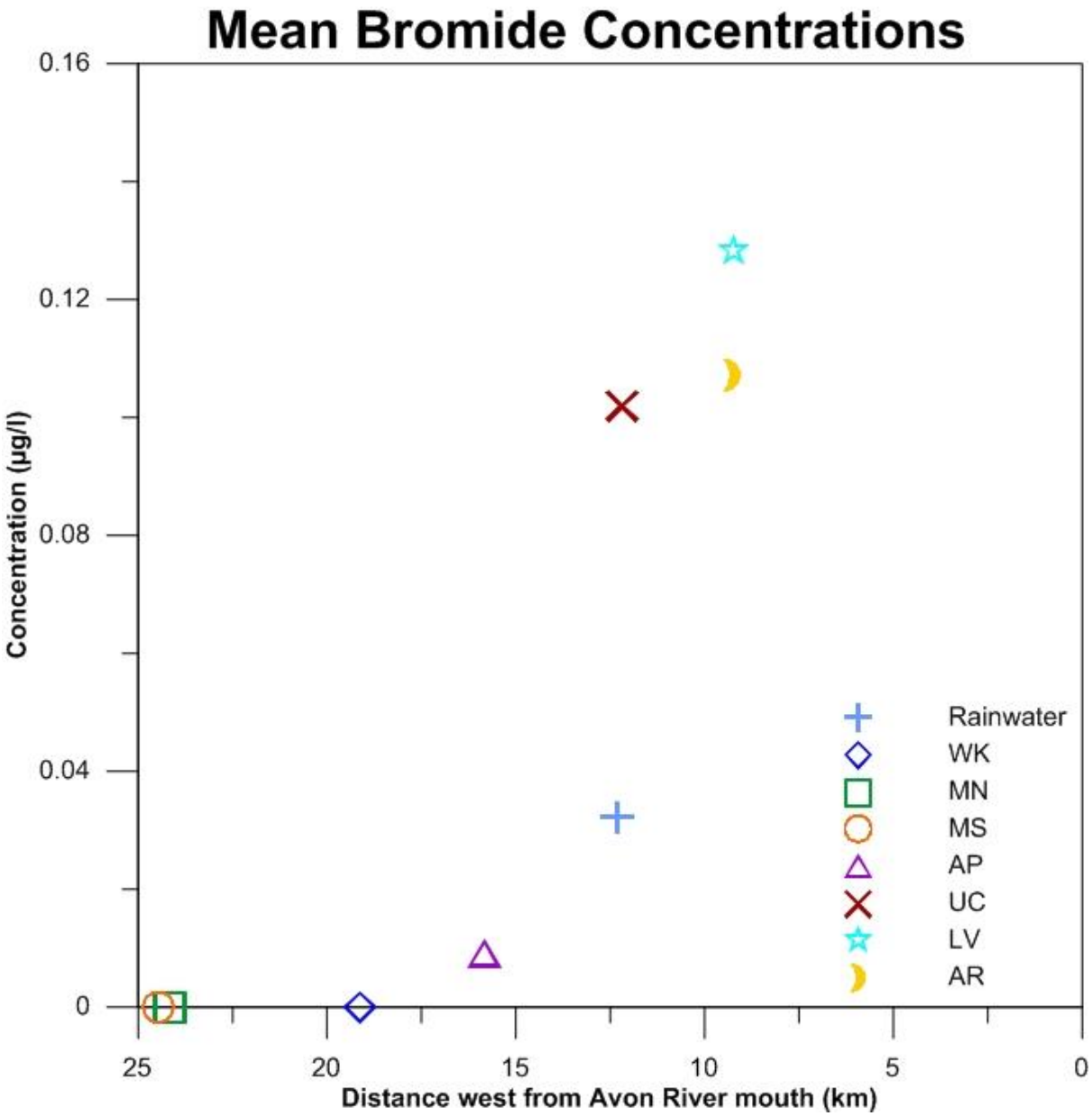


Figure 4.13: Mean bromide concentrations of samples collected from surface water sample sites and rainwater.

Figure 4.14 plots the change in bromide concentration between each site as a function of time. As with previous anions, each site's values have been scaled to emphasise deviations from their respective base line concentrations. These were performed to identify changes in concentrations, in response to rainfall events, and are not indicative of actual concentration values. Bromide concentrations in rainwater are not shown but were correlated separately and are shown in Appendix III.

Deviations from baseline levels generally coincide with rainfall events with variable responses. Sites WK, MN, MS and AP showed minimal response to rainfall events with bromide concentrations below detection levels and therefore unsuitable for tracking groundwater. Changes in concentrations observed at sites UC, LV and AR do not consistently coincide with rainfall events therefore are unlikely to be derived from meteoric water.

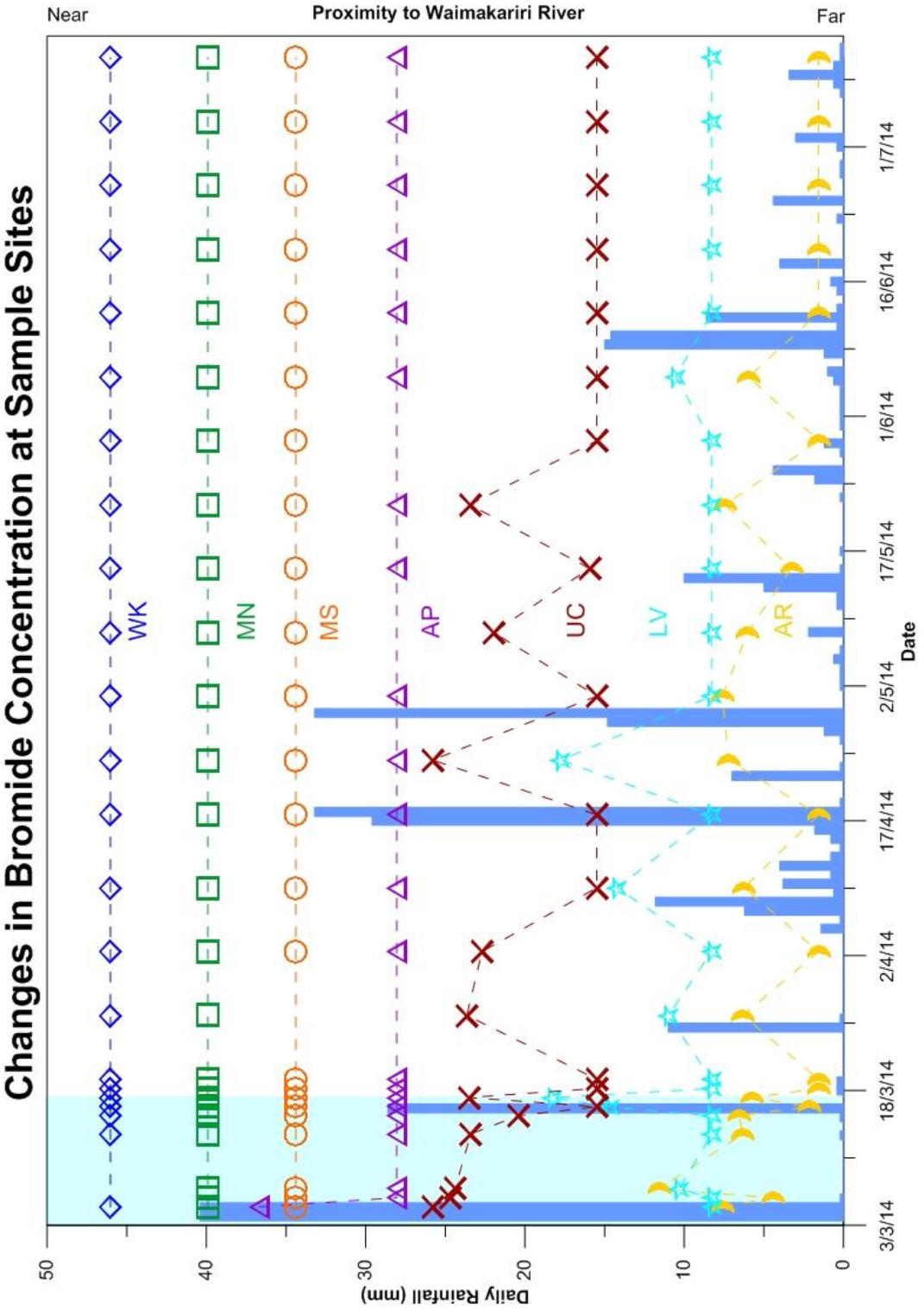


Figure 4.14: Bromide concentration changes at surface water sampling sites. The sites are ordered top to bottom with respect to distance from the Waimakariri River. The underlain blue bar graph is the recorded rainfall for that day and corresponds to the left-hand y-axis. The light blue bar highlights the large rainfall events in March, 2014. Note rainwater concentrations are not represented in the figure.

4.4 RAINFALL RESPONSE

Table 4.9 presents the average values of anion concentrations from gutter water samples collected at around 8:00 pm on July 9th, proximal to each of the streams. Values suggest that road runoff into surface water bodies has a negligible effect on anion concentrations as mean concentrations are a reflection of the anions present in the rainwater.

Mean Concentration of Gutter Water Samples (n=3) and Rainwater				
Anion	**Gutter Water Mean Concentration (mg/l)**	**Gutter Water Standard Deviation**	**Rainwater Mean Concentration (mg/l)**	**Rainwater Standard Deviation**
Chloride	8.78	3.03	8.52	7.79
Nitrate	1.14	1.97	1.08	1.16
Sulfate	2.14	1.22	2.80	2.26
Nitrite	0.04	0.02	0.03	0.03
Fluoride	0.03	0.02	0.08	0.12
Bromide	Below detection level		<0.01	<0.01

Table 4.9: Summary table of mean anion concentrations in gutter water samples and rainwater samples (rounded to 2 decimal places).

Figure 4.15 shows the location of sites used to observe the response of a rainfall event on the anionic concentrations of surface waters.

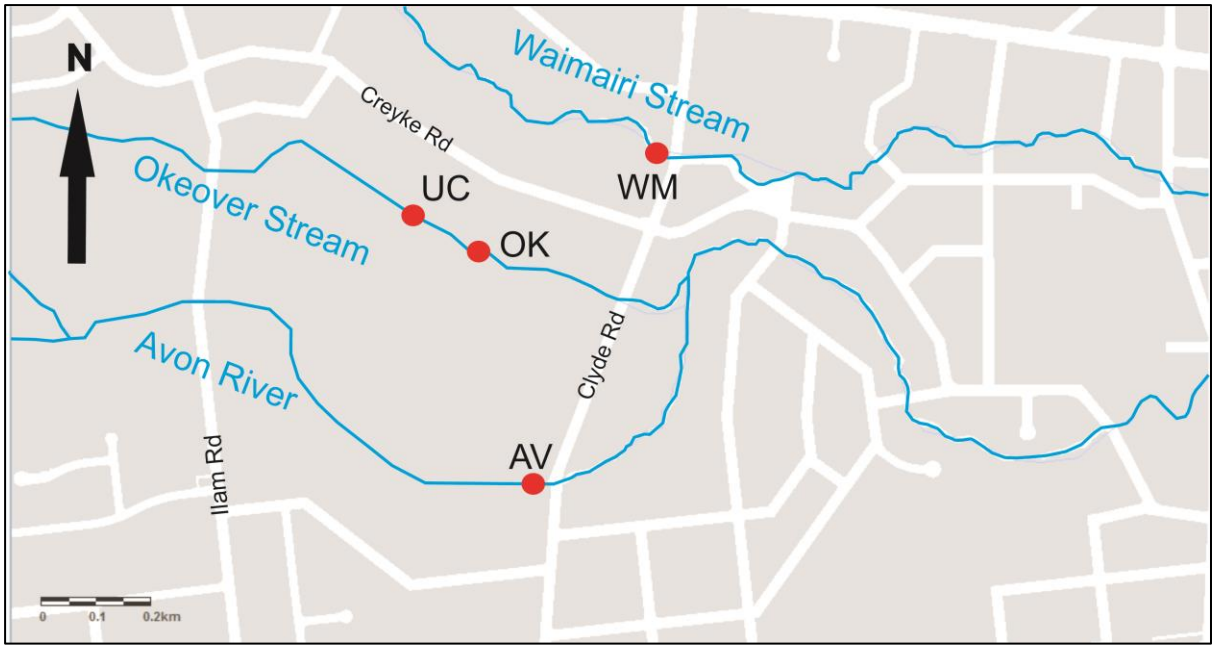


Figure 4.15: Locations of surface water collection sites on the Avon River (AV), Okeover (OK) and Waimairi (WM) streams with the University of Canterbury sample site (UC) as a reference.

Figures 4.16, 4.17 and 4.18 show the anionic response of the Avon River and the Okeover and Waimairi Streams, respectively, to a rainfall event at 8 hour intervals. The gap in data points between July 6 and July 8 is due to a stoppage in sampling as an initially forecast rainfall event did not occur. The dilution of the anion concentrations within the streams and river is visible as a decrease in chloride, nitrate and sulfate concentrations in each of the figures presented. The dilution effect lags behind the rainfall event by a minimum of 8 hours, with the dilution effect lasting a maximum of 16 hours at all three sites.

Note that the lefthand y-axis is used for concentrations of fluoride, nitrite and bromide, and the righthand y-axis is used for concentrations of chloride, nitrate and sulfate.

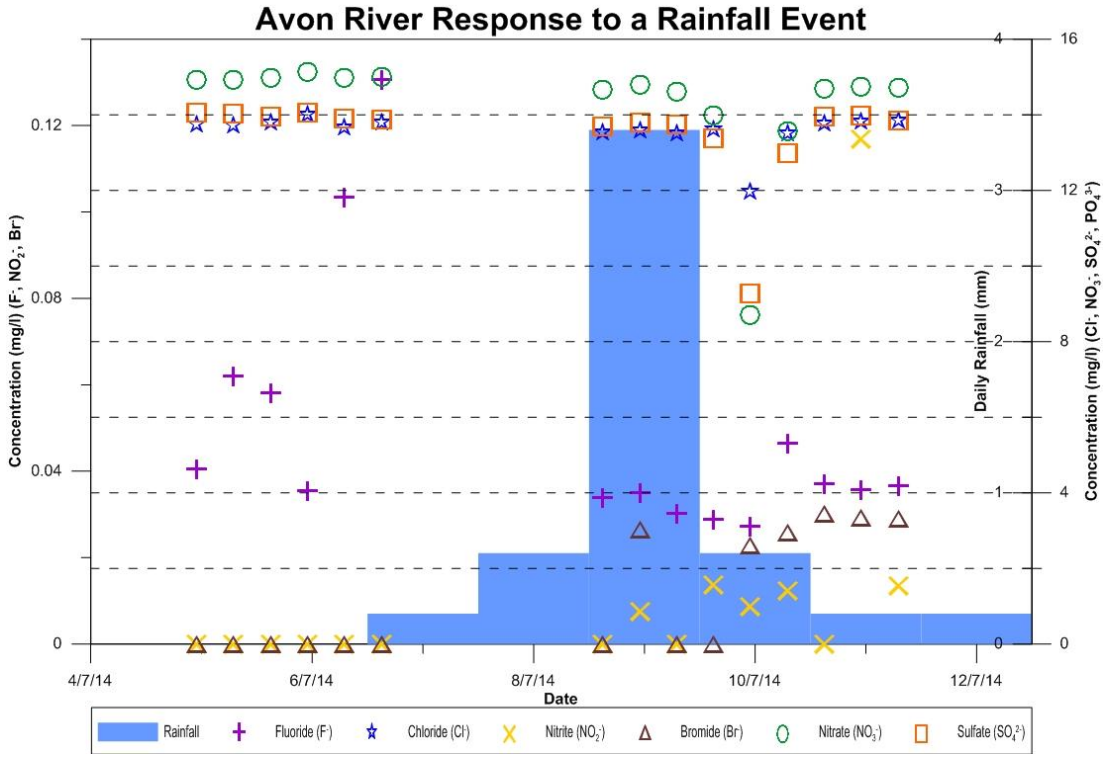


Figure 4.16: The anionic response of the Avon River to a rainfall event sampled at 8 hour intervals.

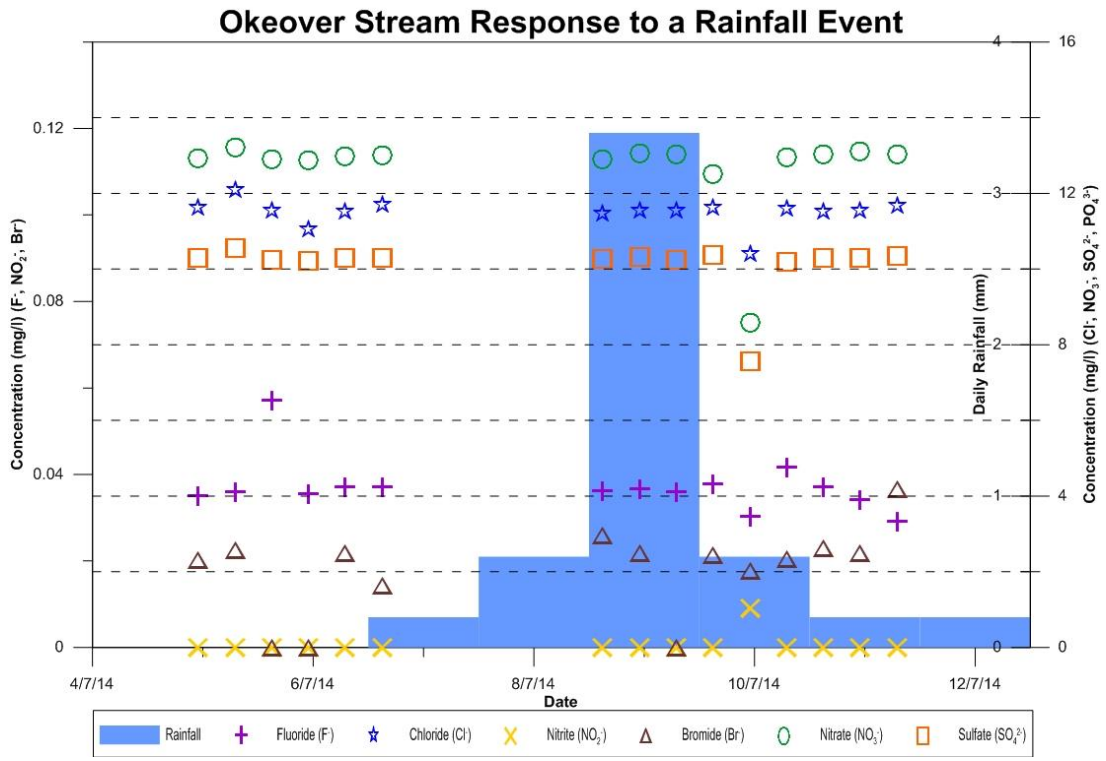


Figure 4.17: The anioinc response of the Okeover Stream to a rainfall event sampled at 8 hour intervals.

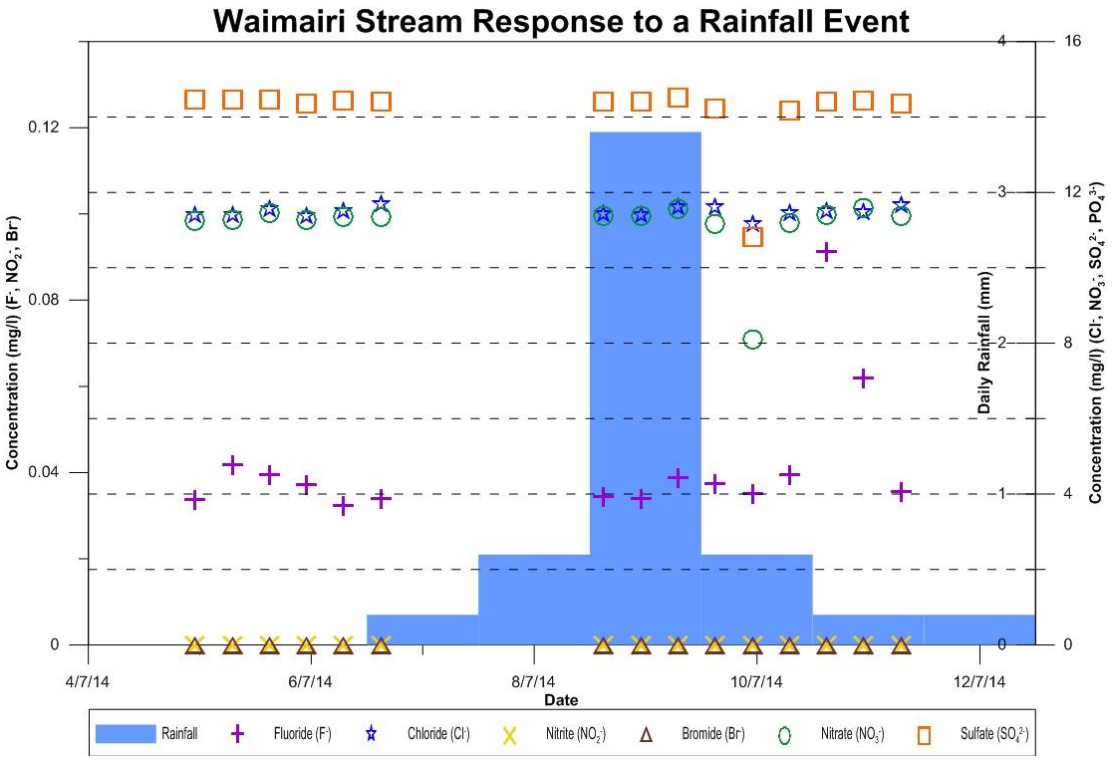


Figure 4.18: The anioinc response of the Waimairi Stream to a rainfall event sampled at 8 hour intervals.

4.5 SUMMARY

Analysis of the surface and meteoric water samples revealed the following key findings:

- The Isotopic compositions of the water samples collected from surface water sites and rainfall lie on or close to the GMWL. The rainwater values generally fall within δD and $\delta^{18}O$ values greater than -55.0‰ and -8.0‰ (V-SMOW), respectively, while surface water site samples had δD and $\delta^{18}O$ values of around -60.0‰ and -8.5‰ (V-SMOW), respectively. This indicates that mean local rainwater is more isotopically 'enriched' than local ground and surface water, conclusive with the findings of Taylor et al. (1989), Blackstock (2011) and Cronin (2012). Isotopic responses at the Avonhead Park (AP), University of Canterbury (UC) and the Avon River (AR) sites were observed more clearly, in response to rainfall events, than other sites. This indicates that these sites are more susceptible to rainwater mixing during rainfall events.
- Chloride, nitrate, sulfate and bromide concentrations were found to increase with increased proximity to the Avon River mouth. Concentrations in rainwater and

Waimakariri River derived groundwater are too low to account for the concentrations observed. Chloride and bromide concentrations are potentially the result of sea spray or salt water mixing or intrusion. The nitrate and sulfate concentrations are potentially the result of fertilizer usage.

- Nitrite concentrations followed the same trend as observed in chloride, nitrate, sulfate and bromide with an increase in concentration with increased proximity to the Avon River mouth. As nitrite concentrations in rainwater was observed as significantly higher than those found at surface water sample sites, the trend may be attributed to a higher levels of rainwater-surface water mixing at sites closer to the Avon River mouth.
- Fluoride concentrations at sample sites decrease as proximity to the Avon River mouth increases. Rainwater samples were observed to have concentrations higher than sample sites. This would suggest that fluoride concentrations cannot be attributed solely to rainwater-surface water mixing as a similar trend to that of nitrite would be expected.
- No distinguishable isotopic or anionic signature was observed in response to the two large rainfall events (March, 2014) used in the attempt to track the groundwater as it flowed through the Waimakariri-Avon River system.
- Observations of the Avon River and the Okeover and Waimairi streams responses to rainfall events show a strong correlation to rainfall with the dilution of chloride, nitrate and sulfate. Dilution effects occur at a minimum of 8 hours following the rainfall event with effects lasting a maximum of 16 hours. Anion concentrations in gutter water samples suggest rainfall as the main contributor, not interaction with the road surface itself, and therefore not likely to influence the anionic concentrations of surface waters where runoff from roads occurs.

CHAPTER 5: DISCUSSION

5.1 INTRODUCTION

The overarching goal of this thesis was to constrain the residence time of the groundwater flowing through the Waimakariri-Avon River system, an important component of the Christchurch aquifer system. By understanding the characteristics of the Waimakariri-Avon River system more accurate estimates can be used to quantify the recharge rate of the Christchurch aquifer system. In order to achieve this surface water samples were collected at set intervals for 4.5 months between March and August, 2014. The samples were analysed for stable isotopic compositions of oxygen and hydrogen as well as their anionic concentrations of chloride, fluoride, nitrate, nitrite, bromide and sulfate. The analysis of the results also aided in achieving the additional objectives of:

- Providing additional evidence of a hydrological connection between the Waimakariri and the Avon River systems,
- Presenting observations of the stable isotopic and geochemical response of surface waters to rainfall events and,
- Identifying the variations in stable isotopic compositions and geochemical concentrations along the Waimakariri-Avon River system and establishing the reasons for the variations.

This chapter presents a discussion on the findings from this thesis and is divided into the following sections:

- The Hydrologic connection of the Waimakariri-Avon River system.

  Discusses evidence of the hydrologic connection of the Waimakariri and Avon Rivers with further evidence of isotopic compositions that support, and supplement, studies already conducted by Taylor et al. (1989), Brown and Weeber (1992), Callander et al. (2005), Blackstock (2011), White et al. (2012) and Cronin (2012).

- Chemical response of surface water to rainfall events.

This section discusses the observations of isotopic composition and anionic concentration fluctuations of surface waters, in response to individual rainfall events, as well as the limitations of the analyses.

- Groundwater residence time in the Waimakariri-Avon River system.

This section discusses the results of stable isotopic composition and anion concentration analyses used to constrain the residence time within the Waimakariri-Avon River system. Possible influences that may have affected the outcome of these analyses are also discussed.

- The use of storm events as groundwater tracers.

This section discusses the use of large, distinct rainfall events as tracers in groundwater systems and their use in further hydrologic investigations.

- Anion profiling of the Waimakariri-Avon River system.

This section discusses the isotopic composition and anionic concentration variation along the course of the Waimakariri-Avon River system. It also discusses the potential spatial influences on the ground and surface water chemistry.

5.2 THE HYDROLOGIC CONNECTION OF THE WAIMAKARIRI-AVON RIVER SYSTEM

Studies by Taylor et al. (1989), Brown and Weeber (1992), Callander et al. (2005), Blackstock (2011), White et al. (2012) and Cronin (2012) have all provided evidence of the connection between the Waimakariri River, Christchurch's groundwater system and the Avon River. Taylor et al. (1989) provided isotopic data and interpretations of $\delta^{18}O$ values within the groundwater beneath Christchurch. Taylor et al. (1989) argued that $\delta^{18}O$ values >-7.0‰ were sourced from precipitation, with $\delta^{18}O$ values between -7.0 and 8.5‰ the result of mixing of precipitation and groundwater. $\delta^{18}O$ values <-8.5‰ were determined to be Canterbury Plains groundwater or Waimakariri River derived.

From the isotopic analysis, conducted on the samples collected, the origin of the surface waters can be interpreted using Taylor et al.'s (1989) framework. As presented in section 4.2, the mean and median rainwater values fell above the -7.0‰ value deduced by Taylor

et al. (1989), verifying that meteoric water, overall, falls above the -7.0‰ $\delta^{18}O$ criterion. Samples taken from Waimakariri River (WK) gave mean and median values <-8.5‰ $\delta^{18}O$, consistent with the findings by Taylor et al. (1989). Sample sites MN, MS, LV and AR all returned mean and median values <-8.5‰ $\delta^{18}O$ suggesting that they are also dominantly recharged by the Waimakariri River. Sample sites AP and UC showed mean and median $\delta^{18}O$ values between -7.0 and -8.5‰ suggesting that they are recharged by a combination of precipitation and groundwater. Figure 5.1 presents the mean isotopic compositions of each of the sites, and precipitation water, against the Global Meteoric Water Line (GMWL), with sites AP (Avonhead Park) and UC (the University of Canterbury) deviating slightly towards the mean precipitation values. The variation observed at certain sites can be largely attributed to the influence of rainfall events. Samples reflecting this variance were likely taken during, or soon after, a rainfall event.

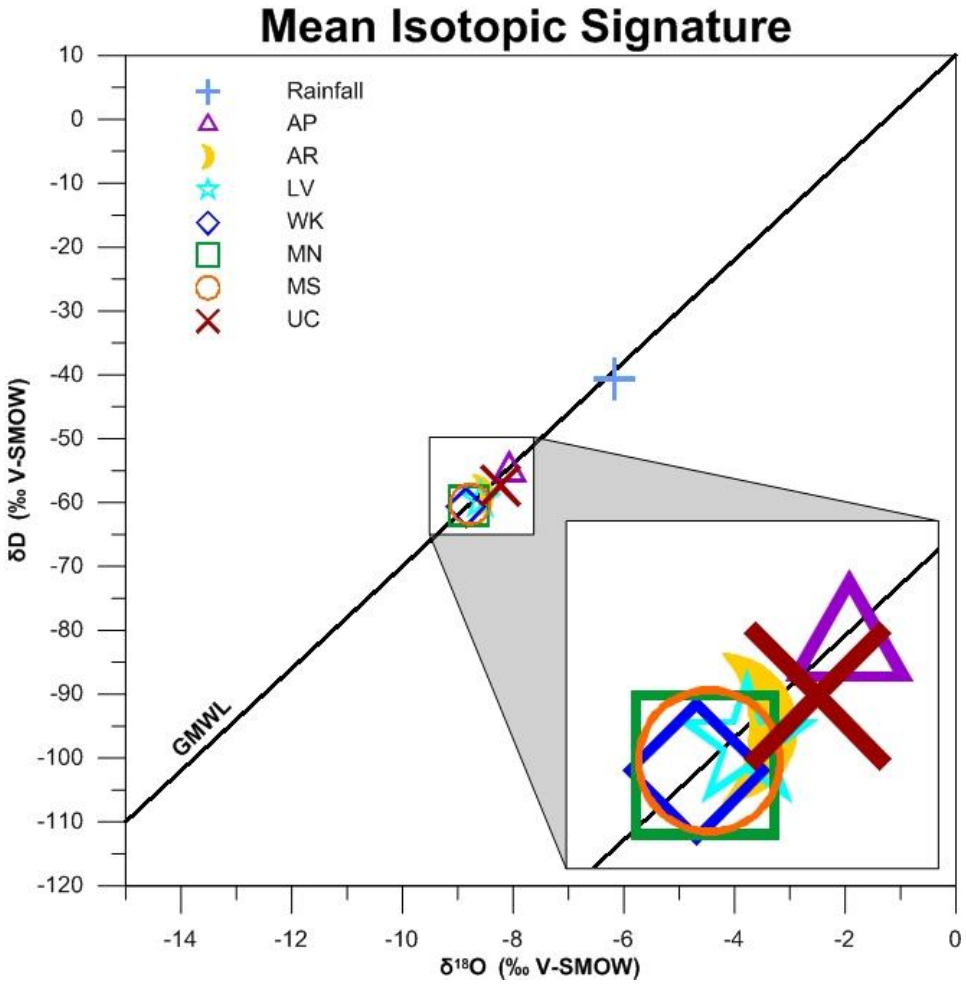


Figure 5.1:

Mean isotopic compositions of samples collected from surface water sites and rainwater samples plotted against the GMWL.

This isotopic data, determined as part of this thesis, reinforces earlier interpretations that surface waters in Christchurch originate from Waimakariri River derived shallow groundwater passing beneath the city. It also shows that the Avonhead Park (AP) and the University of Canterbury (UC) sites are noticeably influenced by rainfall events.

The limitations of this analysis is that it only reflects the period between March and August, 2014 and while the findings may fit the long term trend, it is important to note that the long term trend for each sample site is likely to vary, as will the isotopic composition of rainfall. It should also be noted that the University of Canterbury (UC) sample site had more samples analysed than any other site which may have resulted in some bias. However this could be overcome by normalising the time interval of samplings.

5.3 CHEMICAL RESPONSE OF SURFACE WATER TO RAINFALL EVENTS

5.3.1 Isotopic composition response

As presented in section 4.2, there are various surface water responses to rainfall events. Figure 5.2 displays the $\delta^{18}O$ value for each sample and their respective sample sites. Baseline $\delta^{18}O$ values are observed deviating in correlation with rainfall events suggesting rainfall is the dominant cause of isotopic variation at each of the surface water sites. Sample sites AP, UC and AR are influenced more so than other sites due to higher contribution of rainwater to each sites' baseline flow.

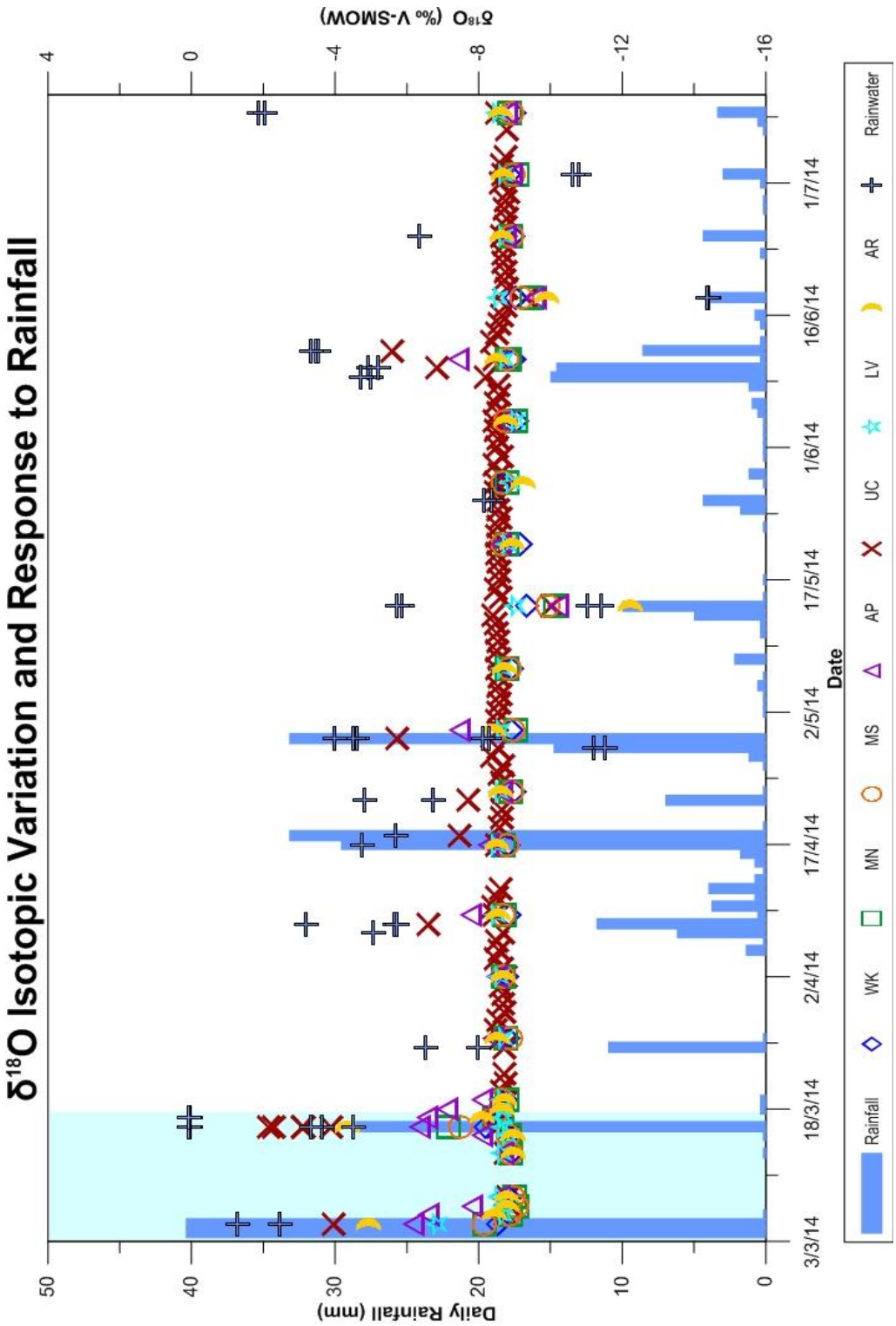


Figure 5.2: $\delta^{18}O$ values of samples versus time and rainfall. The blue bars correlate to daily rainfall and the data points are $\delta^{18}O$ values obtained from samples. The light blue section highlights the large rainfall events in March, 2014.

Also observed is the response of each of the sites to large rainfall events. By observing the two large rainfall events in March, 2014, it is evident that each of the sites, with the exception of the Lake Victoria (LV) sample site, shows a response to rainfall. The Lake Victoria (LV) sample site shows no response to rainfall events as it is a groundwater bore, fed by deeper groundwater than the other surface water sample sites. Deviations observed in the Lake Victoria (LV) samples are attributed to lake levels submerging the groundwater bore pipe used to collect the samples from the site.

Further observations of the $\delta^{18}O$ values also determined that the response was noticeable in days following a large rainfall event. All sites returned near to pre-rainfall isotopic compositions 3 days after a large rainfall event. This suggests that while rainfall has the potential to change the isotopic signature of surface waters during rainfall events, it is quickly flushed through the system and overridden by the base flow Waimakariri River recharge source. Observing other rainfall events, at sites more influenced by rainfall (AP, UC and AR), the isotopic signature of these sites also responds rapidly to rainfall events but they return to their pre-event isotopic composition after 1-2 days following a rainfall event. This suggests that single rainfall events have minimal effects on the long term isotopic signature of surface waters but continuous and ongoing contributions of many rainfall events appear to be responsible for the baseline $\delta^{18}O$ value deviation away from that of its dominant source, Waimakariri River derived shallow groundwater.

5.3.2 Anion concentration response

As presented in sections 4.3 and 4.4, rainfall events appear to cause, at least in part, the fluctuations in surface water anion concentrations. Like isotopic compositions, most rainfall events have a variable effect on anion concentrations. This may be attributed to variations in anion concentrations in rainwater between each rainfall event. It is important to note that rainwater anion concentrations vary spatially and as a result of the chemistry of the vapour mass source (e.g. Ocean derived vapour is more likely to reflect that of ocean chemistry). Also to consider are the variations in precipitation volumes and durations. Higher volume, longer lasting rainfall events are going to have a greater influence on the anion concentrations in surface water as there is more rain water mixing with the base flow water than that of lower volume, short duration rainfall events. Other potential causes of

fluctuating anion concentrations are soil interactions with rainwater. Anions present in soils may be mobilised during rainfall events and transported into surface water bodies. As soil sampling and testing was not conducted near any of the sites, it cannot be verified that this process is, or is not, occurring in regards to the study area.

In most instances isotopic composition and anion concentration fluctuations last only short periods of time 1-2 days following a rainfall event before returning to baseline concentrations. Section 4.4 showed that fluctuations in the anion concentrations lagged behind the rainfall event by a minimum of 8 hours and lasted only a maximum of 16 hours (Figure 5.3). While the event was small in comparison to the large rainfall events in March, 2014, it does further highlight the response rate at which rivers and streams operate.

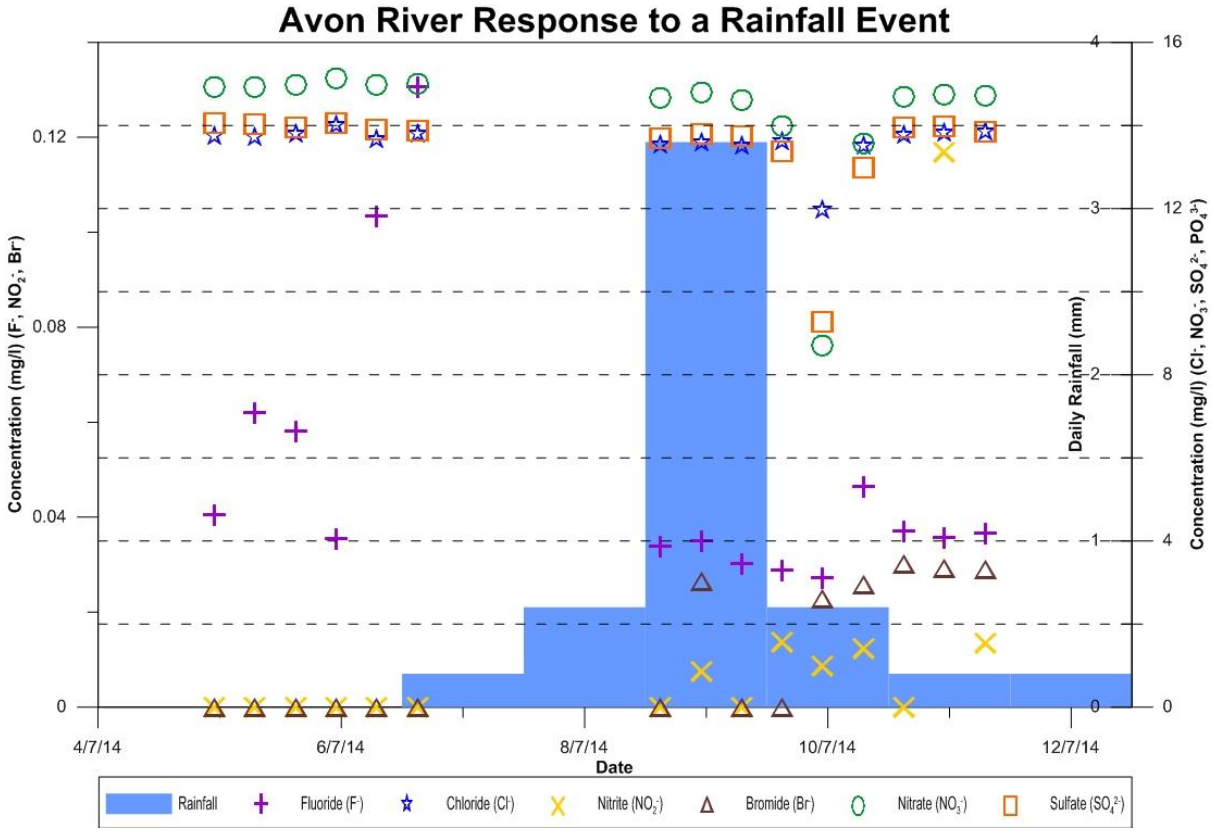


Figure 5.3: The chemical response of the Avon River to a rainfall event sampled at 8 hour intervals.

5.3.3 LIMITATIONS

As stated in the above sections, precipitation can vary spatially and temporally, therefore the concentrations and compositions of the anions and isotopes can also vary in this regard.

Another consideration is the discharge volumes of specific water bodies. Dilution of streams with higher discharges will require a higher volume of rainwater in order to alter the water's composition or concentrations. Inversely, dilution of streams with lower discharges will occur more readily under the influence of the same volume of rainwater. The rainfall values used are 'daily rainfall' values collected from a public weather station in Ilam, Christchurch (Ilam Weather, 2014) and do not distinguish rainfall duration or intensity.

5.4 GROUNDWATER RESIDENCE TIME IN THE WAIMAKARIRI-AVON RIVER SYSTEM

The overarching goal of this thesis was to constrain the residence time of the groundwater flowing through the Waimakariri-Avon River system. Interpretation of the isotopic compositions through time found no distinguishable isotopic fluctuation as a result of the March, 2014 rainfall events passing through each, or any of the sites, in an attempt to track the flow of the groundwater. Subsequent fluctuations observed after the March, 2014 rainfall events have all been attributed to separate rainfall events with isotopic signatures that were reflected in the response of the surface water sample sites, following each rainfall event. Interpretation of the anion concentrations found no definitive deviation from baseline concentrations at surface water sample sites in response to the March, 2014 rainfall events. Any fluctuations in anion concentrations were largely attributed to local rainfall events. Observed fluctuations, not related to local rainfall events, are believed to be the result of other unknown influences on the groundwater system as they did not show the characteristics of the March, 2014 rainfall events or subsequent rainfall events within the sampling period.

The result of the groundwater tracking may be attributed to one or more factors which, potentially, affected the identification of water that entered into the groundwater system as a result of the March, 2014 rainfall events and are discussed below, in section 5.5.

5.5 THE USE OF STORM EVENTS AS ISOTOPIC GROUNDWATER TRACERS

From the observations of the isotopic fluctuations, with respect to time, there appears to be a response in the surface waters' isotopic composition in response to the two storm events at the beginning of the sampling period (March, 2014). The response of the surface waters

to the storm events was also identified in the surface water for at least 2 days following the storm events themselves. This would suggest that storm events, with an isotopic signature that is significantly different from the baseline isotopic composition of the surface water, are useful as isotopic tracers. The issue that may be faced with the usefulness of the tracer arises when taking into account other factors that may affect the isotopic tracer once it enters the groundwater system.

It is possible that, in spite of the large rainfall volumes, contributed by the March, 2014 rainfall events, the dominant recharge source of the groundwater (Waimakariri River) diluted the signature of the rainfall events whilst in the Waimakariri-Avon River system. While in the groundwater system, the storms' rainwater is likely to have mixed with mean Waimakariri River derived groundwater as well as infiltrated rainwater from subsequent rainfall events. Likewise, in the event of its presence at the surface water sampling sites, direct rainfall could have masked the signature of the March, 2014 rainfall events. This would prevent the storms' rainwater from being distinguishable from that of the 'normal' chemistry of the ground and surface waters or rainwater.

It is also possible that the isotopic signature, from the March, 2014 rainfall events, was not observed because it was not collected, due to the frequency of sampling. As shown previously (refer: Section 4.2), the distinct isotopic signature of the March, 2014 rainfall events lasted only 2-3 days at surface water sites, following the rainfall events. Assuming that the signature in the groundwater, from the March, 2014 rainfall events is only identifiable for the same period of time, the isotopic signature may not have been sampled, as the majority of surface water sample sites were only sampled once every 7 days.

Although an idealised groundwater pathway was identified in section 4.2, groundwater can take alternative flow paths. It is possible that the Waimakariri River surface water, that was altered by the March, 2014 rainfall events' rainwater, was taken into the groundwater system but has taken an alternative groundwater flow path. The flow path that was taken may not intersect with any of the surface water sampling sites or simply flowed into a deeper aquifer than the aquifer that feeds the springs associated with the surface water sample sites. Due to the nature of the alternative groundwater flow paths, one of the

springs may have reflected the isotopic signature but as it was not observed at other surface water sample sites it was not identified.

Another possibility is that the altered Waimakariri River water (from the March, 2014 rainfall events) had not had sufficient time to pass through the groundwater system at the time sampling was ceased. Given the known nature of groundwater systems, the isotopic tracer water may still be identifiable within the system. As alluded to by Taylor et al. (1989), the ground water may take up to a year to reach the boundary of the confined zone, which is outside the sampling period undertaken in this thesis. If this were the case, the groundwater residence time could then be constrained to a minimum of 4.5 months.

From the observations of anion concentration fluctuations, with respect to time, there appears to be identifiable responses to the large March, 2014 rainfall events. The response of surface waters to rainfall events can be observed but the effect is short lived with rates of recovery exceeding sampling frequency. The response of the anion concentrations in the surface waters to rainfall events appears to be variable between different anions as well as between individual sites. In many cases fluctuations in anion concentrations are very low (<0.1 mg/l) or quickly recover to baseline anion concentrations making tracking difficult on a weekly, if not daily, time scale. In this particular study, tracking anion concentrations was not found to be a useful method for constraining the residence time of the Waimakariri-Avon River system.

It is therefore important, when considering the use of storm events as isotopic tracers, to have a good understanding of the area's geology including: stratigraphy, structural features (i.e. faults, bedding), material properties (hydraulic conductivity, effective porosity, permeability). It is also important to have a good understanding of the areas hydrology in terms of: aquifer systems, flow rates, hydraulic gradient, subsurface flow paths and the water's sources and origins. And lastly when using natural chemical tracers, it is important to quantify existing compositions and/or concentrations within the hydrogeological system being studied in order to identify the tracer throughout the system. These factors will help to better understand, and quantify, the effects the system will have on the tracer's signature so that sampling can be conducted more effectively in terms of frequency, duration and site selection.

5.6 ANION PROFILING OF THE WAIMAKARIRI-AVON RIVER SYSTEM

Anion concentrations between sample sites varies with proximity to the Avon River mouth. A noticeable change in chloride, nitrate, sulfate and bromide concentrations is observed between the Avonhead Park (AP) and the University of Canterbury (UC) sample sites (Figure 5.4). While the change in anion concentrations is identifiable, isotopic compositions and anion concentrations do not suggest large volume mixing of water from sources other than the Waimakariri River and meteoric water. As mentioned previously (refer: Section 4.5), the change in concentrations may be attributed to salt water/sea spray influences and fertilizer usage interacting with groundwater. Concentrations of fluoride and nitrite are considered to be present at naturally occurring concentrations.

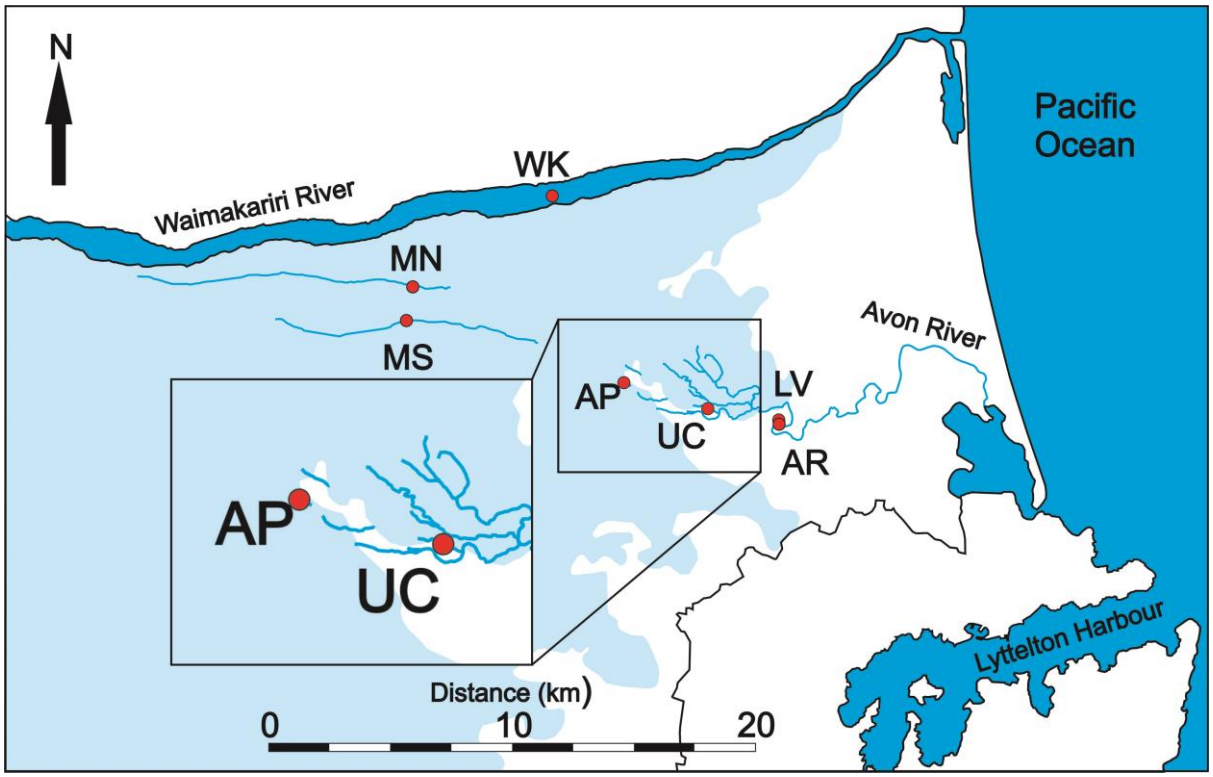


Figure 5.4: Map highlighting the area in which the change in anion concentrations is observed between Avonhead Park (AP) and the University of Canterbury (UC). The Light blue shaded area is the extent of the upper unconfined aquifer with the area east of the boundary part of the confined aquifer system.

5.6.1 Bromide and chloride

The variation in chloride and bromide concentrations observed between surface water sample sites is likely, in part, the result of their proximity to the Avon River mouth (the ocean) and the boundary of the confined aquifer system. The confining layer of marine/estuarine derived sediments (Christchurch Formation) may contain residual concentrations of anions. These may be mobilised by groundwater flow toward the coast, and brought to the surface via a nearby spring. Table 5.1 presents the mean bromide/chloride ratios for all surface water sample sites and sea water. As both chloride and bromide are conservative tracers (non-reactive), the ratios of chloride to bromide at the surface water samples should reflect those found in sea water if sea water is mixing with groundwater (with consideration to the baseline concentrations of chloride and bromide in the groundwater).

Surface Water Sample Site	Mean Bromide concentration (µg/l)	Mean Chloride concentration (mg/l)	Mean Bromide/Chloride ratio
Sea Water	650	18980	3.43×10^{-3}
WK	0	1.06	0
MN	0	1.28	0
MS	0	1.74	0
AP	0.01	3.05	3.28×10^{-4}
UC	0.10	12.57	7.96×10^{-4}
LV	0.13	9.04	1.44×10^{-3}
AR	0.11	11.28	9.75×10^{-4}

Table 5.1: Comparison of bromide/chloride ratios for surface sample sites and sea water.

The comparison of bromide/chloride ratios indicate that ratios of bromide/chloride at surface water sample sites are lower than those of sea water. Therefore it is possible that the source of the chloride and bromide concentrations at the surface water sample sites is from a salt water source but with a higher concentration of chloride which may be attributed to sea spray influences. The decrease in chloride concentration between the

University of Canterbury (UC) and Avon River (AR) sites is potentially due to a dilution effect from other Avon River tributaries with lower chloride levels than those observed at the University of Canterbury. The data still suggests a widely distributed source area as the level of dilution observed would be expected to be greater if the other Avon River tributaries had significantly lower chloride and bromide concentrations.

5.6.2 Nitrate and Sulfate

Nitrate and sulfate concentrations observed at the sites may be attributed, in part, to the use of fertilizers. Elevated nitrate levels are commonly associated with agricultural influences and the use of fertilizers, which also contain sulfate. However elevated nitrate and sulfate concentrations are not present until the University of Canterbury (UC) site, distant from farmland influence. The relative levels of nitrate and sulfate suggest that it is not the influence of salt water. Salt water derived from the Christchurch Formation would likely have similar anion ratios to that of sea water concentrations. Table 5.2 presents mean nitrate and sulfate to chloride concentration ratios for each surface water sample site as well as sea water.

Sample site	Mean Nitrate/Chloride ratio	Mean Sulfate/Chloride ratio
Sea water	3.69×10^{-6}	0.14
Rainwater	0.13	0.33
WK	0.37	4.40
MN	0.10	3.67
MS	0.12	3.85
AP	0.14	1.44
UC	1.05	0.86
LV	1.14	1.25
AR	0.76	0.97

Table 5.2: Ratios of nitrate to chloride and sulfate to chloride of sample sites, rainwater and sea water.

If the nitrate and sulfate anions were attributed to sea water then the chloride ratios should be similar to that of sea water. However the nitrate and sulfate ratios are greater than those found naturally in sea water suggesting an alternate source of the nitrate and sulfate anions. A few potential explanations for this occurrence may be domestic or recreation field use of fertiliser or, potentially, agricultural based fertiliser that directly infiltrates and passes

beneath other sample sites until it is upwelled by a groundwater spring near the University of Canterbury. From the observations in section 6.4, the source of the elevated concentrations is believed to be well integrated into the groundwater system with no fluctuations observed following a rainfall event suggesting it is not likely the result of surface runoff contributions. The concentrations of nitrate and sulfate were also found to be stable with time which suggests a constant and consistent supply of nitrate and sulfate into the groundwater system. Observations of the Avon River (AV), Waimairi (WM) and Okeover (OK) Streams suggest that the source of the nitrate and sulfate is not localised in just one surface water stream. The presence of similar elevated concentrations in each stream suggests that the source of the nitrate and sulfate is having an area-wide effect on the ground and surface water system. Unfortunately the spatial difference between sampling sites AP and UC prevents any conclusive identification of the source, but does identify a potential area in which the source may reside. It is worth mentioning that this same area has been identified by Environment Canterbury (ECan) as potentially being impacted by historic agricultural land-use practices.

Figure 5.5 illustrates the mean concentrations of chloride, nitrate and sulfate between surface water sampling sites showing the change in anion concentrations with respect to proximity to the Avon River mouth. The 'dashed line' in figure 5.5 indicates the large step change in surface water chemistry between Avonhead Park (AP) and the University of Canterbury (UC) and is an important new finding. The relative concentrations of nitrate and sulfate at sites WK, MN, MS and AP suggest that there is a natural source of sulfate within the Waimakariri-Avon River system. If water within the Waimakariri River was mixed with significant surface water runoff from fertilized pastoral sites along its course it would be expected to show higher nitrate concentrations relative to those of sulfate.

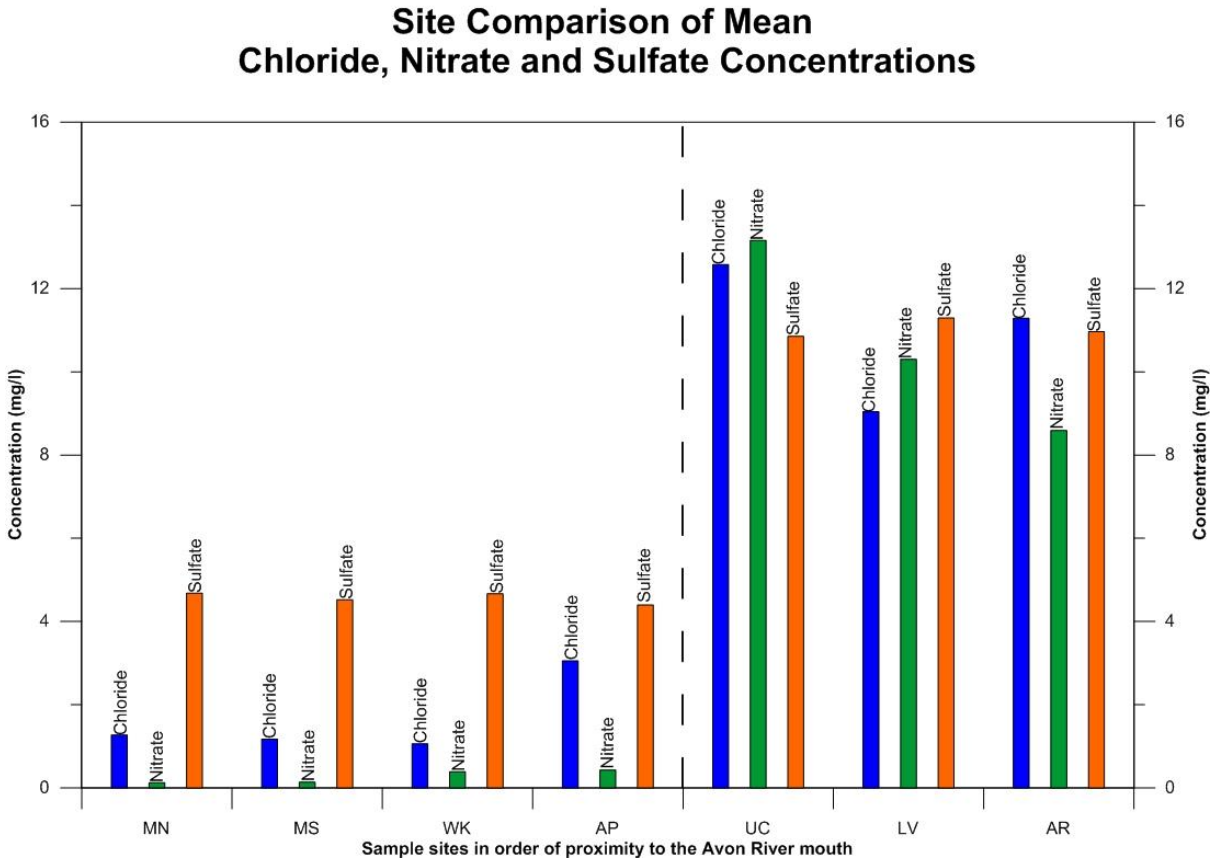


Figure 5.5: Mean concentrations of chloride, nitrate and sulfate at each surface water sampling site. Proximity to the Avon River mouth increases between sites with the left-most site being the furthest away. Dashed line indicates step-change in chemistry.

5.7 SUMMARY

There are 6 key interpretations that are supported by the data presented in this thesis. These interpretations achieve, in part, the aims of this thesis. These key interpretations include:

The isotopic analysis of surface waters and rainwater provided further evidence that the Waimakariri River is the dominant source of ground water beneath the city of Christchurch. The origin of water for many of the surface waters that flow through Christchurch comes from Waimakariri derived shallow groundwater with minor contributions also attributed to rainwater infiltration and recharge.

Rainfall events were shown to have a noticeable effect on surface water chemistry, in many cases the isotopic and anion composition fluctuations correlated to rainfall events. The

effects of rainfall on the surface water chemistry were often only identifiable for a short period of time (<24 hours) following an individual rainfall event. Larger rainfall events (i.e. ex-tropical cyclone Lusi) had noticeable effects lasting 2-3 days.

As a result of sampling, no identifiable trace of the March, 2014 storm events was detected in the surface water samples collected, following the rainfall events, in an attempt to constrain the residence time of groundwater in the Waimakariri-Avon River system. Results are inconclusive as to whether the residence time is greater than, or less, than the sampling period of 4.5 months.

The use of storm events as a means of tracking groundwater was found to be of little use in this study as the signature of the storm was never identified. However the use of this method may be more suited to studies with sampling sites more closely spaced and sampled at higher frequencies.

The use of anions as a tool for tracking groundwater flow was determined to be unreliable in this particular study. The concentrations of naturally occurring anions within the Waimakariri-Avon River groundwater system were too low to be tracked. Rainfall events could be observed but only at high sampling frequencies and the effects of the events were determined to last only a short period of time (<24 hours) before their signature was masked by the dominant recharge source, Waimakariri River derived shallow groundwater.

Profiling of the Waimakariri-Avon River ground water system found anomalous increases in chloride, bromide, nitrate and sulfate concentrations in surface water sampling sites at the University of Canterbury and those closer to the Avon River mouth. The significant increase in chloride and bromide has been attributed to sea spray and potential groundwater interaction with the Christchurch Formation, whose boundary resides close to the University of Canterbury. Nitrate and sulfate concentrations have been attributed to fertilizer use within the urban area however the potential source of the nitrate and sulfate cannot be determined due to the spatial variance between surface water sampling sites. Observations from the Avon River, Waimairi and Okeover streams suggest that the source of the nitrate and sulfate concentrations is having an area-wide effect on local streams. Concentrations of fluoride and nitrite were considered to be of low concentration and naturally occurring.

CHAPTER 6: CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

6.1 CONCLUSIONS

The Waimakariri-Avon River system is an important resource for those living in the city of Christchurch. The main aim of this thesis was to constrain the residence time of the groundwater flowing through the Waimakariri-Avon River system. Additionally, this thesis also aimed to:

- Provide additional evidence of the connection between the Waimakariri River and the Avon River,
- Present observations of the isotopic and anionic response of surface water to rainfall events, and also,
- Identify isotopic and anionic variations along the Waimakariri-Avon River system and establish the reasons for them.

The residence time for the groundwater flowing through the Waimakariri-Avon River system was unable to be constrained within this thesis' findings. The isotopic tracer that was used, derived from two large rainfall events in March, 2014, was not identified at any of the surface water sites that were sampled, following the rainfall events. The reason for this may be explained by the isotopic tracer being diluted as it mixed with groundwater already in the system. Additionally the isotopic tracer may have been masked during sampling by subsequent rainfall events. The sampling frequency used may also have been too low in order to capture the isotopic tracer as it moved through the system. Previously known subsurface flow paths were used to plan surface water collection sites, as they suggested the prominent flow path, but the isotopic tracer may have flowed along a different flow path.

This thesis supported and provided additional evidence of the connection between the Waimakariri River and the Avon River. There is a clear isotopic similarity between the Waimakariri River and the surface water sites that were sampled. The mean isotopic composition of local rainfall was determined to be distinctly different from that of the isotopic composition of the Waimakariri River. Surface water samples displayed isotopic compositions more closely reflecting that of the Waimakariri River than local rainfall

indicating the Waimakariri River as the dominant recharge source of shallow groundwater, with minor contributions from rainfall.

Variability in isotopic composition and anionic concentration of surface waters was observed in response to individual rainfall events. The response to a rainfall event was identifiable as a deviation from the mean isotopic composition and anionic concentration, coinciding with rainfall events. The response of the surface waters to rainfall events was identified as lasting less than 24 hours for a small individual event, after rainfall had ceased, but responses to the large rainfall events in March, 2014 were observed for up to 3 days after rainfall stopped. Due to the short lived nature of rainfall effects on the surface waters of Christchurch, accurate tracking of rainfall events would require high frequency sampling over short time periods.

Isotopic variation along the course of the Waimakariri-Avon River system was shown to reflect, predominantly, Waimakariri River derived water. Contributions of local rainfall are recognised in the isotopic signature of surface waters and increases with increased proximity to the Avon River mouth. This indicates that the further away from the Waimakariri River the surface water is, the greater the contribution it has from rainfall to its baseline composition. Anionic concentration observations of the Waimakariri-Avon River system identified a large step-change in chloride, bromide, nitrate and sulfate anions between Avonhead Park and the University of Canterbury (Figure 6.1). The cause of the increase in chloride concentrations are believed to be the result of salt water mixing of deeper groundwater interacting with the marine and estuarine sands that act as a confining layer between the upper unconfined aquifer and deeper aquifers. It also suggests a widely distributed source area as concentrations do not become diluted at the Avon River site, at Hagley Park, from the addition of other tributaries, which would be expected if they did not have similarly high chloride and bromide concentrations. Nitrate and sulfate concentrations are believed to be the result of fertilizer usage but the direct source is unknown. Environment Canterbury (ECan) has identified the area as being possibly impacted by past agricultural land-use practices and may explain the large increase observed between these two sites.

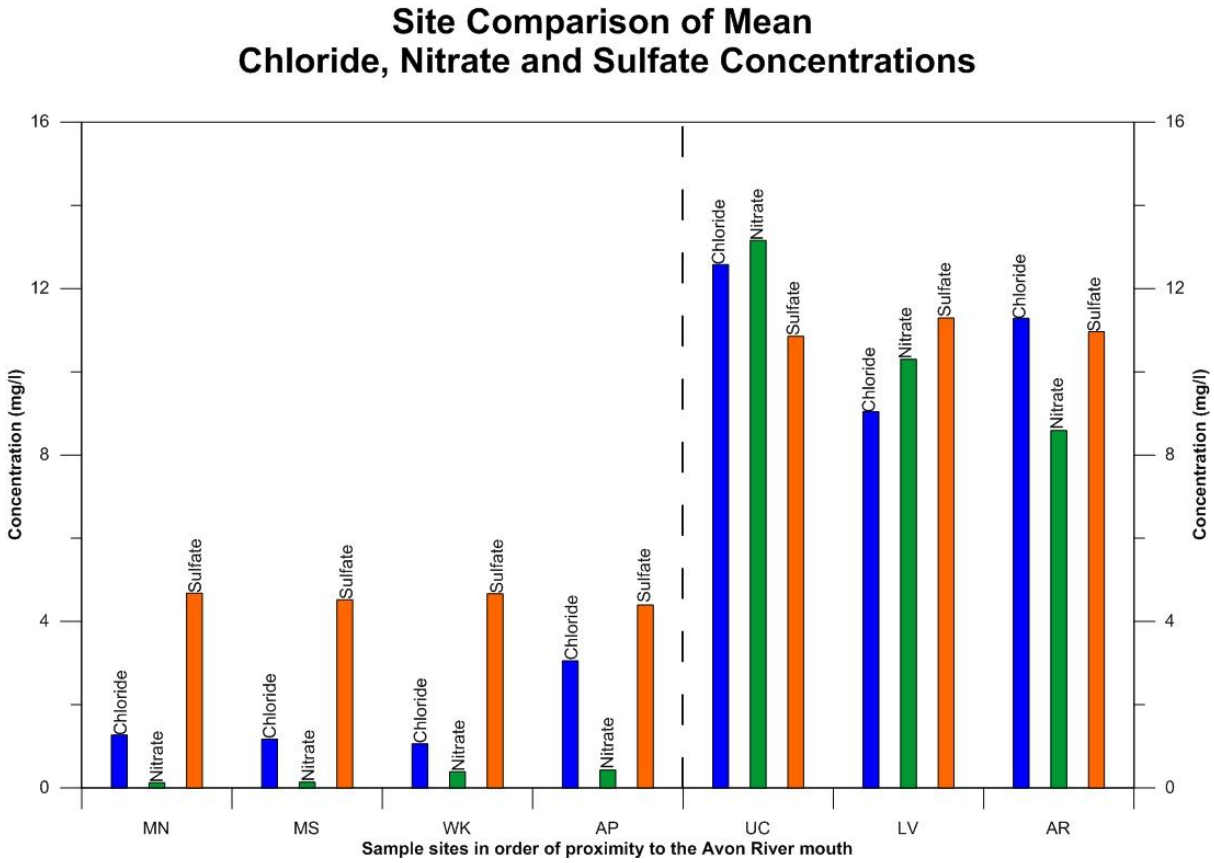


Figure 6.1: Mean concentrations of chloride, nitrate and sulfate at each surface water sampling site. Proximity to the Avon River mouth increases between sites with the left-most site being the furthest away. Dashed line indicates step-change in chemistry.

6.2 FUTURE RESEARCH DIRECTIONS

Understanding the various factors influencing the Waimakariri-Avon River groundwater system is crucial for the management and monitoring of the groundwater resource. Future groundwater tracking attempts should aim to sample more frequently and over a longer period of time. Sampling from the water table itself should also be used closer to the Waimakariri River in order to reduce the effect dilution has on the tracer itself. The use of artificial tracers could also be considered but only when the effects of such tracers have no detrimental effects to the overall quality of the ground and surface waters themselves.

To better understand the effects of rainfall events on the alteration of surface water chemistry, further investigation is need. Ideally sampling would be used before, during and after rainfall events of variable durations and intensities, as well as at high sampling

frequencies to identify and measure the effects precipitation has on local surface water bodies.

Another important area of research is the determination of the source and extent of the increased chloride, bromide, nitrate and sulfate concentrations near the University of Canterbury. This should include a more detailed investigation with soil sampling and higher density profiling of the Waimairi and Okeover Streams, the Avon River and the area west of the University, as well as other tributaries of the Avon River.

CHAPTER 9: BIBLIOGRAPHY

Appelo, C., Postma, D., 1993. Geochemistry, groundwater and pollution. A.A.Balkema, Rotterdam, Netherlands.

Avery, G Jr., Willey, J., Kieber, R., 2001. Diurnal variations in major rainwater components at a coastal site in North Carolina. Atmospheric Environment, V.35, No. 23, p. 3927-3933.

Blackstock, J., 2011. Isotope study of moisture sources, recharge areas, and groundwater flow paths within the Christchurch groundwater system. Unpublished Master of science thesis, University of Canterbury.

Bowen, R., 1986. Groundwater. Elsevier Science Publishing Co., Inc., New York, USA.

Brown, L., Weeber, J., 1992. Geology of the Christchurch urban area. Institute of Geological & Nuclear Sciences, Lower Hutt, New Zealand.

Callander, P., Thorley, M., Lough, H., Williams, H., Kininmonth, M., Henderson, B., 2005. Groundwater flow modelling for groundwater quality assessments in Christchurch city. Retrieved on October 6, 2014 from www.pdp.co.nz/documents/2005callanderetal1.pdf

City University of New York (CUNY), 2011. Availability of water. Retrieved on October 10, 2014 from http://www.geography.hunter.cuny.edu/~tbw/ncc/Notes/chapter12.humans.env/world.water.sources.jpg

Clark, I., Fritz, P., 1997. Environmental isotopes in hydrogeology. CRC Press LLC, New York, USA.

Cronin, M., 2012. The Stable Isotopic and Anionic Composition of the Avon and Heathcote River Systems, Christchurch, New Zealand: a study of lowland spring-fed rivers in a seismically active environment. Unpublished Master of science thesis, University of Canterbury.

Davie, T., 2008.Fundamentals of hydrology. Taylor & Francis, New York, USA.

Domenico, P., Schwartz, F., 1990. Physical and chemical hydrogeology. John Wiley and Sons, Inc., New York, USA.

Environment Canterbury (ECan), 2002. Christchurch-West Melton groundwater quality: A review of groundwater quality monitoring data from January 1986 to March 2002. Retrieved on October 6, 2014 from http://*ecan.govt.nz/publications/Reports/U0247a.pdf*

Environment Canterbury (ECan), 2010. An overview of the state and trends in water quality of Canterbury's rivers and streams. Retrieved on October 6, 2014 from http://ecan.govt.nz/publications/Reports/overview-state-trend-water-quality-canterbury-rivers-streams.pdf

Faure, G., 1986. Principles of Isotope Geology. 2nd ed, John Wiley & Sons, Inc., New Jersey, USA.

Fetter, C., 1999. Contaminant Hydrology. 2nd ed, Prentice-Hall, Inc., New Jersey, USA.

Fetter, C., 2001. Applied hydrogeology. Prentice-Hall Inc., New Jersey, USA.

Geotechnical Extreme Events Reconnaissance (GEER), 2011. Geotechnical reconnaissance of the 2011 Christchurch, New Zealand earthquake. Retrieved on October 28, 2014 from http://www.geerassociation.org/GEER_Post%20EQ%20Reports/Christchurch_2011/Cover_Christchurch_2011.html

Haast, J., 1879. Geology of the provinces of Canterbury and Westland, New Zealand. Times Office, Christchurch, New Zealand.

Heath, R, 1983. Basic groundwater hydrology. U.S. Geological Survey, Virginia, USA.

Hoefs, J., 1987. Stable isotope geochemistry. Springer-Verlag, Berlin, Germany.

Ilam Weather, 2014. Daily temperature reports. Retrieved on February 14, 2015 from: http://ilamweather.com/weather_history.php?name=wxtempdetail&period=detail&year=2014

Institute of Geological & Nuclear Sciences (GNS), 2008. Geology of the Christchurch area. GNS Science, Lower Hutt, New Zealand.

Institute of Geological & Nuclear Sciences (GNS), 2013. Median water table elevation in Christchurch and surrounding area after the 4 September 2010 Darfield Earthquake, Version 1. Geology of the Christchurch area. GNS Science, Lower Hutt, New Zealand.

Kazemi, G., Lehr, J., Perrochet, P., 2006. Groundwater age. John Wiley & Sons, Inc., New Jersey, USA.

Kendall, C., McDonnell, J., 1998. Isotope tracers in catchment hydrology. Elsevier BV, Oxford, UK.

Lu, X., 2009. Lu X. (2009). Simulation of the upper Waimakariri River catchment by observed rain & radar reflectivity. Unpublished Master of science thesis, Lincoln University.

Penn State University (PSU), 2014. Basic chemistry: atoms and ions. Retrieved on November 10, 2014 from http://www.personal.psu.edu/staff/m/b/mbt102/bisci4online/chemistry/chemistry2.htm

Piccaro, 2010. ChemCorrect^{TM}- Solving the Problem of Chemical Contaminants in H_20 Stable Isotope Research. Retrieved on November 11, 2014 from http://www.picarro.com/assets/docs/Picarro_-_ChemCorrect_White_Paper.pdf

Schmidt, G., Bigg, g., Rohling, E., 1999. Global seawater oxygen-18 database - v1.21. Retrieved on January 20, 2015 from http://data.giss.nasa.gov/o18data/

Sharp, Z., 2007. Principles of stable isotope geochemistry. Pearson Education/Prentice Hall, New Jersey, USA.

Soliman, M., LaMoreaux, P., Memon, B., Assaad, F., LaMoreaux, J., 1998. Environmental Hydrology. Lewis Publishers, Boca Raton, Florida, USA.

Stanford University, 2014. Mineral makeup of seawater. Retrieved on October 24, 2014 from https://web.stanford.edu/group/Urchin/mineral.html

Stute, M., 2002. Story line for the B2C ground water exhibit. Retrieved on October 16, 2014 from http://www.ldeo.columbia.edu/~martins/pfaz/images/gaining_losing_stream.gif

Taylor, C.B., Wilson, D.D., Brown, L.J., Stewart, M.K., Burden, R.J., Brailsford, G.W., 1989. Sources and flow of north Canterbury plains groundwater. New Zealand: Journal of Hydrology, v. 106, no. 3-4, p. 311–340, doi: 10.1016/0022-1694(89)90078-4.

Walesh, S., 1989. Urban surface water management. John Wiley & Sons, Inc., New York, USA.

White, P., 2009. Avon River springs catchment, Christchurch City, New Zealand. Australian Journal of Earth Sciences: An International Geoscience Journal of the Geological Society of Australia, 56(1): pp 61-70.

White, P., Kovacova, E., Zemansky, G., Jebbour, N., Moreau-Fournier, M., 2012. Groundwater-surface water interaction in the Waimakariri River, New Zealand, and groundwater outflow from the river bed. Journal of Hydrology (NZ), New Zealand Hydrological Society, 51 (1): pp 1-24.

Younger, P., 2007. Groundwater in the environment: An introduction. Blackwell publishing Ltd., Oxford, UK.

APPENDICES

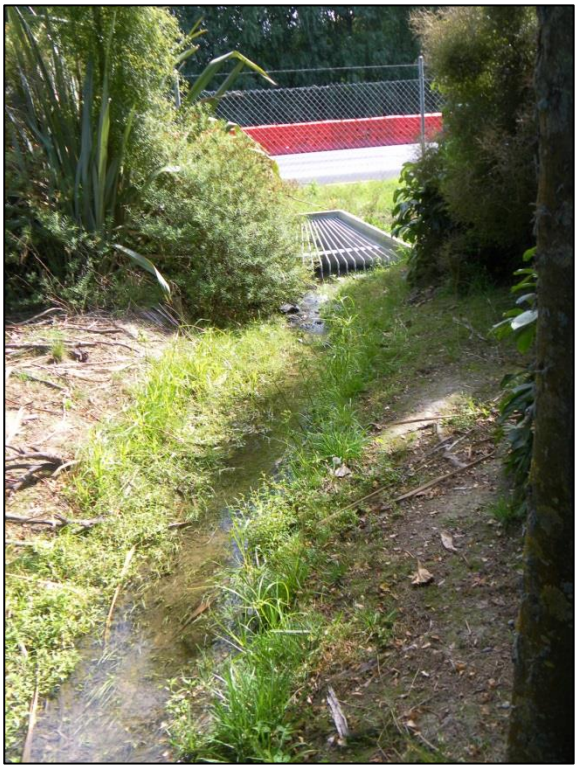
APPENDIX I: PHOTOS

SURFACE WATER SAMPLE SITES

Left: Surface water sample site at the Waimakariri River (WK), looking toward the northern bank. Haul Rd is out of shot, behind and to the right of the photo's field of view. Power pylons offer a point of reference.

Left: Surface water sample site at the northern agricultural water race (MN) along Chattertons Rd, looking toward the west. Chattertons Rd is out of shot, directly behind the photo's field of view.

Left: Surface water sample site at the southern agricultural water race (MS) along Chattertons Rd, looking toward the west. Chattertons Rd is out of shot, directly behind the photo's field of view.



Left: Surface water sample site at Avonhead Park (AP), with Russley Rd in the background, looking toward the west. Avonhead Park fields are directly behind the photo's field of view.

Left: Surface water sample site at the University of Canterbury (UC), along Okeover Stream. The geology/biology carpark is directly behind the photo's field of view.

Left: Surface water sample site along the Avon River (AR), at Hagley Park, looking south. The North Hagley carpark is directly behind the photo's field of view. The North Hagley bridge crossing is to the left of the photo's field of view.

Left: Surface water sample site at the western edge of Lake Victoria (LK), at Hagley Park. Arrow indicates the groundwater bore used to collect samples. Photo is taken looking toward the east.

RAINWATER COLLECTOR

Left: Rainwater collector used on the top of Puaka-James Hight Library. (Similar set up used on the western side of the Von Haast building)

APPENDIX II: SAMPLE DATA

SURFACE WATER SITE: WAIMAKARIRI RIVER (WK)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
WK01	5/03/2014	-8.55	0.04	-56.21	0.35	12.18	0.0501	1.5078	0	0	0.4969	5.1035	6.86
Waimakariri River March 8, 2014	8/03/2014	-8.84	0.08	-60.91	0.39	9.83							
WK04	13/03/2014	-8.92	0.04	-60.30	0.25	11.03	0.0511	1.3983	0	0	0.5303	5.4924	7.18
WK05	15/03/2014	-8.84	0.05	-60.34	0.18	10.39	0.0507	1.2078	0	0	0.3927	5.4446	6.96
WK06	16/03/2014	-8.19	0.04	-55.80	0.13	9.75	0.0507	1.4101	0.0072	0	0.326	5.0071	6.63
WK07	17/03/2014	-8.58	0.07	-59.42	0.29	9.22	0.0412	1.2303	0.0436	0	0.333	5.2225	6.92
WK08	18/03/2014	-8.65	0.05	-59.82	0.16	9.35	0.0502	1.2258	0	0	0.4576	5.2577	7.04
WK09	19/03/2014	-8.75	0.05	-60.67	0.43	9.36	0.0518	1.2267	0	0	0.4295	5.3146	7.06
WK10	26/03/2014	-8.83	0.10	-60.80	0.28	9.83	0.0512	1.1346	0	0	0.3414	5.2838	7.1
WK11	2/04/2014	-8.77	0.06	-61.30	0.56	8.83	0.0514	1.0885	0	0	0.232	5.3976	7.15
WK12	9/04/2014	-8.83	0.06	-61.10	0.43	9.53	0.0339	1.1682	0	0	0.2562	5.3476	7.02
WK13	17/04/2014	-8.83	0.04	-62.60	1.05	8.01	0.0361	1.2747	0.0129	0	0.2619	5.285	7.16
WK14	23/04/2014	-8.99	0.07	-61.81	0.72	10.11	0.0335	1.1396	0	0	0.4388	4.556	7.2
WK15	30/04/2014	-8.91	0.08	-61.33	0.21	9.94	0.0491	1.0656	0	0	0.4334	4.3952	6.72
WK16	7/05/2014	-8.93	0.03	-60.47	0.84	10.98	0.0405	0.824	0	0	0.2722	3.6838	6.73
WK17	14/05/2014	-9.32	0.02	-63.52	0.05	11.04	0.0331	0.8521	0	0	0.4118	4.2431	6.76
WK18	21/05/2014	-9.17	0.00	-61.59	0.93	11.75	0.047	0.95	0	0	0.5153	4.6017	6.87
WK19	28/05/2014	-8.66	0.02	-58.29	0.63	11.02	0.0368	1.0291	0	0	0.3084	3.737	7.13
WK20	4/06/2014	-9.05	0.02	-61.11	0.06	11.27	0.0357	0.9023	0	0	0.3641	3.9674	6.97
WK21	11/06/2014	-8.99	0.02	-60.23	0.50	11.66	0.0435	0.09482	0	0	0.4224	3.7072	6.9
WK22	18/06/2014	-9.01	0.05	-61.94	0.22	10.12	0.0411	1.0281	0	0	0.5134	4.1923	6.75
WK23	25/06/2014	-8.96	0.07	-61.06	0.48	10.66	0.0414	0.9348	0	0	0.486	4.3268	6.81
WK24	2/07/2014	-8.84	0.03	-60.71	0.40	10.03	0.0244	0.8062	0	0	0.2839	3.459	6.9
WK25	9/07/2014	-8.97	0.05	-62.32	0.45	9.45	0.0417	0.9079	0	0	0.4715	4.2448	7.05

SURFACE WATER SITE: NORTHERN AGRICULTURAL WATER RACE ALONG CHATTERTONS RD (MN)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
MN01	5/03/2014	-8.14	0.09	-52.04	0.20	13.07	0.0478	3.8206	0	0	0.2807	4.7057	6.64
MN02	6/03/2014	-8.87	0.04	-58.78	0.65	12.15	0.0564	1.2171	0	0	0	5.5809	7.86
MN03	7/03/2014	-9.06	0.04	-61.05	0.33	11.43	0.0514	1.2888	0	0	0.0392	5.3357	7.11
nw Waimak Drain March 8, 2014	8/03/2014	-8.98	0.07	-60.80	0.22	11.07							
MN04	13/03/2014	-8.89	0.07	-60.37	0.22	10.73	0.0569	1.165	0	0	0	5.4292	7.5
MN05	15/03/2014	-8.86	0.08	-60.38	0.39	10.50	0.0553	1.1138	0	0	0	5.3831	7.04
MN06	16/03/2014	-7.13	0.04	-48.11	0.23	8.96	0.0467	1.9853	0	0	0.0536	4.3263	6.67
MN07	17/03/2014	-8.44	0.09	-57.92	0.27	9.60	0.0504	1.1432	0	0	0.0729	5.0388	6.94
MN08	18/03/2014	-8.63	0.08	-59.93	0.16	9.07	0.0525	1.1711	0	0	0.0492	5.1429	7
MN09	19/03/2014	-8.76	0.06	-60.87	0.07	9.22	0.0537	1.1773	0	0	0.018	5.2442	7.08
MN10	26/03/2014	-8.75	0.07	-60.13	0.26	9.89	0.0499	1.1889	0	0	0	5.1382	7.2
MN11	2/04/2014	-8.68	0.06	-60.72	0.40	8.70	0.0456	0.9958	0	0	0	5.3394	7.26
MN12	9/04/2014	-8.72	0.09	-60.75	0.29	8.98	0.0346	1.1293	0	0	0.0447	5.3473	7.08
MN13	17/04/2014	-8.68	0.10	-62.26	0.69	7.20	0.036	1.4382	0	0		5.2586	7.32
MN14	23/04/2014	-8.89	0.09	-61.25	0.63	9.85	0.0332	1.1052	0.0097	0	0.2019	4.4891	7.35
MN15	30/04/2014	-9.02	0.05	-61.02	0.48	11.10	0.0496	1.1791	0	0	0.1455	4.325	6.9
MN16	7/05/2014	-8.79	0.02	-61.78	0.34	8.51	0.0346	0.8271	0	0	0	4.0621	6.96
MN17	14/05/2014	-10.12	0.04	-70.08	0.22	10.86	0.0285	1.3035	0	0	0.213	3.5512	6.77
MN18	21/05/2014	-8.79	0.07	-60.63	0.31	9.66	0.059	1.0703	0	0	0.1057	5.6238	7.05
MN19	28/05/2014	-8.78	0.04	-59.25	#DIV/0!	11.00	0.0306	0.9126	0	0	0.1598	3.7038	6.92
MN20	4/06/2014	-9.02	0.13	-60.25	0.06	11.94	0.0287	0.9005	0	0	0.2315	4.2387	7.03
MN21	11/06/2014	-8.84	0.20	-60.49	0.57	10.22	0.1326	0.9537	0	0	0.3331	3.8224	6.21
MN22	18/06/2014	-9.45	0.08	-67.05	0.17	8.58	0.0571	1.6462	0	0	0.3873	4.1876	6.94
MN23	25/06/2014	-8.88	0.10	-60.46	0.58	10.58	0.0467	0.909	0	0	0.232	4.2435	6.91
MN24	2/07/2014	-9.07	0.05	-62.60	0.34	9.95	0.0216	1.3056	0	0	0.1899	3.3585	6.81
MN25	9/07/2014	-8.85	0.03	-61.71	0.21	9.12	0.0275	0.925	0	0	0.2323	4.1638	7.12

SURFACE WATER SITE: SOUTHERN AGRICULTURAL WATER RACE ALONG CHATTERTONS RD (MS)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
MS01	5/03/2014	-8.15	0.04	-52.42	0.72	12.80	0.0461	3.2735	0.0084	0	0.0303	4.7101	6.8
MS02	6/03/2014	-8.85	0.02	-59.88	0.40	10.94	0.0559	1.2961	0	0	0	5.6547	8.08
MS03	7/03/2014	-9.04	0.04	-60.91	0.11	11.39	0.0544	1.2398	0	0	0	5.314	7.32
SW Waimak Drain March 8, 2014	8/03/2014	-8.96	0.05	-60.35	0.22	11.29							
MS04	13/03/2014	-8.89	0.03	-59.87	0.08	11.25	0.0549	1.1353	0	0	0	5.4466	8.37
MS05	15/03/2014	-8.79	0.02	-60.27	0.18	10.08	0.0551	1.2066	0	0	0	2.2249	6.88
MS06	16/03/2014	-7.49	0.03	-50.22	0.14	9.69	0.048	1.4547	0	0	0	4.4372	6.64
MS07	17/03/2014	-8.44	0.05	-58.05	0.18	9.50	0.051	1.1804	0.0041	0	0.09	5.0612	6.96
MS08	18/03/2014	-8.62	0.04	-59.81	0.15	9.13	0.0535	1.1629	0	0	0.0752	5.1726	7.04
MS09	19/03/2014	-8.64	0.05	-60.90	0.30	8.21	0.055	1.1646	0	0	0.0457	5.2356	7.05
MS10	26/03/2014	-8.87	0.05	-60.68	0.71	10.25	0.0498	1.0589	0.0112		0	5.3176	7.45
MS11	2/04/2014	-8.66	0.07	-60.58	0.05	8.70	0.0436	0.9945	0	0	0.0474	5.3853	7.3
MS12	9/04/2014	-8.69	0.04	-60.86	0.18	8.63	0.0398	1.1478	0.0132	0	0.0953	5.2609	7.07
MS13	17/04/2014	-8.76	0.09	-62.74	0.69	7.37	0.0369	1.245	0	0	0.0774	5.1273	7.38
MS14	23/04/2014	-8.91	0.04	-61.26	0.65	10.03	0.0342	1.1189	0	0	0.2569	4.5391	7.48
MS15	30/04/2014	-8.96	0.03	-61.23	0.19	10.42	0.0514	1.1055	0	0	0.2616	4.3445	6.8
MS16	7/05/2014	-8.86	0.04	-60.94	0.02	9.94	0.0378	0.7934	0	0	0	3.5253	6.73
MS17	14/05/2014	-9.93	0.09	-67.83	0.57	11.62	0.036	1.0374	0.0002	0	0.2499	3.8253	7.76
MS18	21/05/2014	-8.67	0.10	-61.24	0.01	8.13	0.0314	0.9863	0	0	0.2338	4.7848	7.11
MS19	28/05/2014	-8.68	0.08	-58.70	0.32	10.72	0.0584	0.9831	0	0	0.2579	3.5892	6.83
MS20	4/06/2014	-8.73	0.08	-60.06	0.89	9.80	0.0339	0.8899	0	0	0.2393	4.174	6.94
MS21	11/06/2014	-8.78	0.06	-58.81	0.54	11.40	0.0217	0.9629	0	0	0.3492	3.7938	6.99
MS22	18/06/2014	-9.18	0.04	-63.77	0.23	9.70	0.0584	1.0666	0	0	0.3693	4.2271	6.94
MS23	25/06/2014	-8.92	0.03	-60.94	0.29	10.46	0.0319	0.9277	0	0	0.2878	4.22924	6.89
MS24	2/07/2014	-8.96	0.08	-61.21	0.73	10.47	0.0301	1.0124	0	0	0.2367	3.5448	6.86
MS25	9/07/2014	-8.91	0.05	-62.04	0.31	9.26	0.0378	0.9101	0	0	0.2729	4.1965	7.09

SURFACE WATER SITE: AVONHEAD PARK (AP)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
AP01	5/03/2014	-6.16	0.06	-33.47	0.23	15.83	0.0428	11.7459	0	0.0204	3.6457	5.1605	6.25
AP02	6/03/2014	-6.59	0.09	-39.60	0.97	13.14	0.041	8.1136	0	0	0	4.7247	6.43
AP03	7/03/2014	-7.81	0.06	-51.44	0.06	11.07	0.0452	2.9317	0	0	0	4.8849	6.5
Avonhead Park March 8, 2014	8/03/2014	-8.55	0.06	-58.09	0.21	10.32							
AP04	13/03/2014	-8.66	0.07	-58.32	0.12	10.98	0.0545	1.253	0	0	0	4.8088	6.72
AP05	15/03/2014	-8.07	0.06	-55.19	0.29	9.37	0.0561	2.286	0	0	0	5.5163	6.7
AP06	16/03/2014	-6.35	0.01	-42.08	0.23	8.71	0.0501	5.8807	0	0	1.8492	4.4832	6.39
AP07	17/03/2014	-6.56	0.04	-43.13	0.59	9.32	0.0379	4.9379	0.0093	0	0.0672	4.2842	6.57
AP08	18/03/2014	-7.12	0.06	-48.67	0.07	8.30	0.0483	2.4351	0	0	0.0226	4.0201	6.64
AP09	19/03/2014	-8.09	0.06	-56.88	0.14	7.80	0.0535	1.2811	0	0	0	4.5924	6.69
AP10	26/03/2014	-8.41	0.01	-59.33	0.94	7.92	0.0479	2.4474				5.3899	6.84
AP11	2/04/2014	-8.49	0.09	-59.41	0.10	8.47	0.0442	0.9318	0	0	0	5.0247	6.91
AP12	9/04/2014	-7.77	0.06	-54.03	0.40	8.16	0.0342	3.2321	0.0205	0	0.0373	4.7635	6.66
AP13	17/04/2014	-8.24	0.10	-59.17	0.28	6.75	0.0379	2.1337	0	0		5.1073	7.02
AP14	23/04/2014	-8.64	0.03	-57.88	0.42	11.27	0.0347	1.8384	0	0	0.0447	4.5599	6.87
AP15	30/04/2014	-7.45	0.10	-50.29	0.12	9.33	0.0405	5.9014	0	0	0.3398	3.5768	6.45
AP16													
AP17	14/05/2014	-10.22	0.04	-73.38	0.21	8.35	0.0339	2.7993	0.0057	0	1.3569	2.7519	6.44
AP18	21/05/2014	-8.60	0.08	-60.33	0.51	8.48	0.042	0.9491	0	0	0.0162	4.209	6.61
AP19													
AP20	4/06/2014	-8.66	0.07	-59.85	0.48	9.42	0.0233	0.932	0	0	0.1099	4.1054	6.83
AP21	11/06/2014	-7.41	0.04	-50.01	0.13	9.25	0.0203	1.8931	0	0	0.4407	3.2369	6.84
AP22	18/06/2014	-9.57	0.08	-68.45	0.23	8.12	0.0571	2.0628	0	0	0.6096	3.7978	6.74
AP23	25/06/2014	-8.76	0.09	-59.77	0.62	10.29	0.0297	0.9343	0	0	0.1297	4.0967	6.75
AP24	2/07/2014	-8.92	0.06	-61.67	0.18	9.70	0.0323	1.5566	0	0	0.287	3.8238	6.9
AP25	9/07/2014	-8.76	0.07	-60.57	0.41	9.51	0.0276	1.7424	0	0	0.1063	4.1778	6.64

Note: Samples AP16 and AP19 were not collected due to insufficient surface water flow.

SURFACE WATER SITE: OKEOVER STREAM, UNIVERSITY OF CANTERBURY (UC)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
UC01	5/03/2014	-3.95		-17.67		13.94	0.0204	13.4693	0	0.0292	3.5401	5.4646	6.18
UC02	6/03/2014	-8.73		-59.63		10.24	0.0361	14.0931	0	0.026	15.8128	12.2162	6.19
UC03	7/03/2014	-8.88	0.08	-59.52	0.55	11.50	0.0409	14.0103	0	0.0252	15.5546	11.9436	6.07
OKEOVER (travis)	8/03/2014	-8.81	0.04	-60.25	0.27	10.24							
UC04	13/03/2014	-8.74	0.04	-59.58	0.17	10.37	0.0302	13.8699	0.0084	0.0224	16.046	11.788	6.27
UC05	15/03/2014	-8.81	0.06	-60.10	0.21	10.40	0.037	13.4309		0.014	15.5071	11.6022	6.58
OKEOVER (11:45; 16-03-2014)	16/03/2014	-3.11	0.02	-12.49	0.37	12.43							
OKEOVER (14:00; 16-03-02014)	16/03/2014	-2.13	0.07	-7.41	0.43	9.64							
OKEOVER (16:00; 16-03-2014)	16/03/2014	-2.30	0.08	-9.81	0.23	8.56							
OKEOVER (9:40; 16-03-2014)	16/03/2014	-3.90	0.02	-18.04	0.26	13.12							
UC06	16/03/2014	-3.09	0.04	-17.85	0.19	6.83	0.0188	7.7004	0.0051	0	3.3647	4.5872	6.22
OKEOVER (10:00; 17-03-2014)	16/03/2014	-8.54	0.05	-57.09	0.42	11.22							
UC07	17/03/2014	-8.45	0.03	-57.76	0.18	9.80	0.0367	14.0273	0	0.0228	14.7619	11.9363	6.5
UC08	17/03/2014	-8.59	0.05	-60.32	0.22	8.42	0.0361	13.5717	0	0	15.4485	11.6643	6.53
UC09	18/03/2014	-8.59	0.09	-60.12	0.18	8.61	0.0368	13.4371	0	0	15.3269	11.5657	6.48
UCAA	19/03/2014	-8.68	0.03	-60.44	0.06	8.99							
UCAB	20/03/2014	-8.62	0.04	-60.05	0.23	8.92							
UCAC	21/03/2014	-8.74	0.06	-60.43	0.19	9.49							
UCAD	22/03/2014	-8.72	0.07	-61.24	0.62	8.49							
UCAF	25/03/2014	-8.71	0.04	-60.09	0.29	9.61							
UC10	26/03/2014	-8.59	0.06	-60.27	0.41	8.46	0.0276	13.3626	0	0.0231	14.6107	11.3664	6.35
UCAG	27/03/2014	-8.47	0.13	-59.87	0.45	7.90							
UCAH	28/03/2014	-8.54	0.04	-60.99	0.08	7.35							
UCAI	29/03/2014	-8.72	0.03	-59.21	0.36	10.51							
UCAJ	30/03/2014	-8.68	0.14	-61.05	0.56	8.39							
UCAK	31/03/2014	-8.67	0.04	-60.33	0.41	9.05							
UCAL	1/04/2014	-8.62	0.05	-61.35	0.30	7.58							
UC11	2/04/2014	-8.73	0.09	-60.27	0.05	9.59	0.0274	13.4666	0.004	0.0204	15.4401	11.9454	6.29
UCAM	3/04/2014	-8.65	0.12	-60.77	0.52	8.40							
UCAN	4/04/2014	-8.48	0.02	-59.16	0.17	8.68							
UCAO	5/04/2014	-8.57	0.05	-59.71	0.54	8.84							
UCAD	6/04/2014	-8.50	0.02	-59.53	0.37	8.51							
UCAQ	7/04/2014	-8.68	0.09	-59.24	0.51	10.19							
UCAR	8/04/2014	-6.58	0.05	-43.84	0.20	8.81							
UC12	9/04/2014	-8.43	0.04	-59.99	0.83	7.46	0.022	13.3805	0	0	14.8759	11.921	6.17

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
UCAS	10/04/2014	-8.40	0.10	-58.49	0.22	8.69							
UCAT	11/04/2014	-8.49	0.05	-58.83	0.27	9.09							
UCAU	12/04/2014	-8.62	0.06	-60.21	0.49	8.72							
UC13	17/04/2014	-8.48	0.06	-60.97	0.24	6.90	0.0238	12.1272	0	0	13.2331	10.3035	6.27
UCAZ	18/04/2014	-7.45	0.05	-51.04	0.04	8.59							
UCBA	19/04/2014	-8.55	0.05	-58.35	0.77	10.06							
UCBB	20/04/2014	-8.65	0.03	-59.70	0.19	9.53							
UCBC	21/04/2014	-8.65	0.05	-59.70	0.24	9.51							
UCBD	22/04/2014	-7.71	0.03	-51.36	0.44	10.35							
UC14	23/04/2014	-8.67	0.07	-59.96	0.21	9.40	0.0952	12.6893	0.0327	0.0292	13.8092	11.2939	6.41
UCBE	24/04/2014	-8.63	0.06	-59.32	0.31	9.73							
UCBF	25/04/2014	-8.57	0.05	-59.38	0.43	9.21							
UCBG	26/04/2014	-8.67	0.12	-59.63	0.63	9.76							
UCBH	27/04/2014	-8.36	0.07	-58.65	0.73	8.19							
UCBI	28/04/2014	-8.54	0.06	-59.51	0.34	8.85							
UCBJ	29/04/2014	-5.72	0.10	-36.39	0.20	9.40							
UC15	30/04/2014	-8.58	0.03	-58.23	0.93	10.42	0.0407	13.9666	0	0	14.1344	12.9448	6.31
UCBK	1/05/2014	-8.49	0.10	-60.02	0.31	7.87							
UCBL	2/05/2014	-8.55	0.09	-60.75	0.32	7.64							
UCBM	3/05/2014	-8.58	0.07	-60.64	0.25	8.01							
UCBN	4/05/2014	-8.62	0.04	-60.97	0.29	7.98							
UCBO	5/05/2014	-8.52	0.06	-61.28	0.36	6.88							
UCBP	6/05/2014	-8.58	0.03	-60.74	0.22	7.88							
UC16	7/05/2014	-8.50	0.06	-61.23	0.21	6.75	0.0272	12.3597	0.0006	0.0184	13.7102	11.2153	6.38
UCBQ	8/05/2014	-8.58	0.09	-60.63	0.18	8.00							
UCBR	9/05/2014	-8.49	0.07	-60.78	0.33	7.13							
UCBS	10/05/2014	-8.54	0.03	-61.01	0.23	7.27							
UCBT	11/05/2014	-8.50	0.04	-60.39	0.27	7.59							
UCBU	12/05/2014	-8.46	0.06	-60.58	0.24	7.11							
UCBV	13/05/2014	-8.39	0.08	-60.43	0.31	6.72							
UC17	14/05/2014	-10.03	0.03	-72.55	0.27	7.73	0.0267	9.8894	0.0001	0.0013	10.2466	9.1274	6.21
UCBW	15/05/2014	-8.59	0.03	-61.55	0.58	7.20							
UCBX	16/05/2014	-8.48	0.09	-60.88	0.42	6.94							
UCBY	17/05/2014	-8.58	0.05	-60.68	0.21	7.96							
UCBZ	18/05/2014	-8.56	0.07	-61.24	0.22	7.22							
UCCA	19/05/2014	-8.53	0.07	-61.16	0.37	7.11							
UCCB	20/05/2014	-8.49	0.09	-60.78	0.37	7.14							

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
UC18	21/05/2014	-8.52	0.04	-61.40	0.45	6.80	0.039	12.4234	0	0.0226	13.805	11.3123	6.25
UCCC	22/05/2014	-8.49	0.00	-60.89	0.31	7.06							
UCCD	23/05/2014	-8.52	0.02	-60.95	0.25	7.21							
UCCE	24/05/2014	-8.60	0.10	-61.47	0.17	7.34							
UCCF	25/05/2014	-8.52	0.13	-61.32	0.37	6.87							
UCCG	26/05/2014	-8.52	0.04	-60.61	0.19	7.59							
UCCH	27/05/2014	-8.47	0.05	-60.54	0.52	7.25							
UC19	28/05/2014	-8.46	0.05	-61.08	0.23	6.59	0.0372	12.4453	0.0467	0	13.7164	11.4533	6.76
UCCI	29/05/2014	-8.57	0.04	-61.01	0.17	7.57							
UCCJ	30/05/2014	-8.44	0.08	-61.01	0.38	6.51							
UCCK	31/05/2014	-8.63	0.09	-61.21	0.27	7.83							
UCCL	1/06/2014	-8.51	0.11	-61.32	0.18	6.76							
UCCM	2/06/2014	-8.54	0.02	-61.37	0.19	6.96							
UCCN	3/06/2014	-8.48	0.08	-61.02	0.22	6.82							
UC20	4/06/2014	-8.45	0.06	-61.48	0.13	6.08	0.0664	12.2112	0	0	13.5234	11.2732	6.51
UCCO	5/06/2014	-8.52	0.12	-60.32	0.22	7.87							
UCCP	6/06/2014	-8.46	0.05	-60.42	0.24	7.25							
UCCQ	7/06/2014	-8.56	0.13	-60.71	0.22	7.75							
UCCR	8/06/2014	-8.54	0.04	-60.81	0.16	7.51							
UCCS	9/06/2014	-8.20	0.08	-57.96	0.28	7.66							
UCCT	10/06/2014	-6.83	0.07	-46.02	0.27	8.63							
UC21	11/06/2014	-8.43	0.04	-59.50	0.32	7.98	0.0222	12.9452	0	0	13.3307	12.3961	6.51
UCCU	12/06/2014	-5.57	0.09	-33.34	0.10	11.23							
UCCV	13/06/2014	-8.36	0.05	-59.87	0.39	7.01							
UCCW	14/06/2014	-8.50	0.07	-60.24	0.38	7.76							
UCCX	15/06/2014	-8.58	0.09	-60.53	0.14	8.12							
UCCY	16/06/2014	-8.64	0.04	-60.62	0.40	8.49							
UCCZ	17/06/2014	-8.73	0.01	-60.43	0.05	9.41							
UC22	18/06/2014	-9.34	0.05	-67.69	0.48	7.01	0.0284	11.1043	0	0	11.8833	10.3972	6.63
UCDA	19/06/2014	-8.76	0.02	-60.43	0.29	9.68							
UCDB	20/06/2014	-8.69	0.09	-60.16	0.08	9.36							
UCDC	21/06/2014	-8.73	0.07	-60.41	0.26	9.42							
UCDD	22/06/2014	-8.68	0.06	-60.74	0.33	8.66							
UCDE	23/06/2014	-8.66	0.03	-60.49	0.29	8.77							
UCDF	24/06/2014	-8.72	0.03	-60.69	0.24	9.09							
UC23	25/06/2014	-8.65	0.06	-61.41	0.52	7.76	0.0215	11.6655	0	0	12.7759	10.7581	6.29
UCDG	26/06/2014	-8.75	0.08	-60.81	0.33	9.16							

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
UCDH	27/06/2014	-8.78	0.03	-60.33	0.49	9.88							
UCDI	28/06/2014	-8.69	0.08	-60.84	0.30	8.71							
UCDJ	29/06/2014	-8.73	0.07	-60.69	0.11	9.14							
UCDK	30/06/2014	-8.83	0.02	-61.17	0.07	9.44							
UCDL	1/07/2014	-8.62	0.14	-60.01	0.13	8.92							
UC24	2/07/2014	-8.66	#DIV/0!	-60.97	#DIV/0!	8.29							
UC24	2/07/2014	-8.80	0.07	-62.06	0.11	8.33	0.0268	11.0975	0	0	11.7714	10.1116	6.27
UCDM	3/07/2014	-8.63	0.02	-59.64	0.70	9.39							
UCDN	4/07/2014	-8.75	0.05	-60.11	0.04	9.89							
UCDQ	7/07/2014	-8.79	0.08	-60.55	0.65	9.76							
UC25	9/07/2014	-8.50	0.08	-61.09	0.39	6.91	0.0328	11.605	0	0	12.7109	10.717	7.1

SURFACE WATER SITE: LAKE VICTORIA (LK)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
LV01	5/03/2014	-6.83	0.06	-47.95	0.28	6.67	0.0605	8.4968	0	0.0254	2.6289	7.1585	6.67
LV02	6/03/2014	-8.67	0.08	-58.84	0.61	10.50	0.0522	9.0292	0	0.0347	10.39	11.2731	6.5
LV03	7/03/2014	-8.70	0.02	-59.38	0.13	10.20	0.0454	9.0391	0.0048	0.02517	10.3976	11.3161	6.36
Lk Victoria (pipe) March 8, 2014	8/03/2014	-8.56	0.05	-58.63	0.30	9.83							
LV04	13/03/2014	-8.62	0.03	-59.07	0.16	9.90	0.0521	9.0368	0	0.0185	10.45	11.3338	6.36
LV05	15/03/2014	-8.76	0.02	-59.43	0.15	10.65	0.0574	9.0479	0	0.0301	10.4257	11.2458	6.47
LV06	16/03/2014	-8.62	0.04	-60.07	0.33	8.89	0.0501	9.1193	0.0151	0.0169	10.3349	11.411	6.6
LV07	17/03/2014	-8.66	0.08	-60.35	0.25	8.95	0.0537	9.136	0.0236	0.0191	10.2706	11.4172	6.59
LV08	18/03/2014	-8.61	0.04	-60.33	0.16	8.58	0.0498	9.0778	0	0	10.5981	11.4463	7.02
LV09	19/03/2014	-8.64	0.08	-60.43	0.30	8.73	0.0511	9.1485	0	0	10.5911	11.4297	6.69
LV10	26/03/2014	-8.66	0.06	-60.19	0.33	9.06	0.0484	9.1519	0.0064	0.0206	10.6453	11.6485	6.59
LV11	2/04/2014	-8.58	0.10	-60.15	0.12	8.52	0.0406	8.9877	0	0.0163	10.4434	11.4611	6.53
LV12	9/04/2014	-8.48	0.01	-59.52	0.54	8.31	0.0407	9.1599	0.014	0	10.3038	11.5459	6.42
LV13	17/04/2014	-8.48	0.03	-60.58	0.14	7.25	0.034	9.2508	0	0	10.5666	11.5204	6.55
LV14	23/04/2014	-8.56	0.03	-59.69	0.20	8.79	0.0433	9.1354	0.0223	0.0255	10.577	11.6409	7.18
LV15	30/04/2014	-8.60	0.07	-58.94	0.51	9.83	0.0433	9.0742	0	0	10.7126	11.6187	6.46
LV16	7/05/2014	-8.64	0.04	-60.18	0.67	8.97	0.0478	9.1063	0	0	10.8035	11.7323	6.47
LV17	14/05/2014	-9.02	0.10	-60.77	0.70	11.39	0.0592	9.0737	0	0.022	10.731	11.6106	6.51
LV18	21/05/2014	-8.77	0.05	-60.95	0.62	9.20	0.0405	9.0448	0	0.0202	10.7235	11.5288	6.37
LV19	28/05/2014	-8.89	#DIV/0!	-59.86	#DIV/0!	11.28	0.0556	9.0697	0	0	10.8411	11.4632	7.28
LV20	4/06/2014	-9.02	#DIV/0!	-60.46	#DIV/0!	11.69	0.0702	9.0101	0.0053	0.0219	10.8635	11.4561	7.13
LV21	11/06/2014	-8.71	0.04	-60.06	0.36	9.60	0.0361	9.0566	0	0.0245	10.8287	11.4638	6.74
LV22	18/06/2014	-8.52	0.02	-60.56	0.27	7.61	0.0441	9.0703	0	0	10.9879	11.5895	6.63
LV23	25/06/2014	-8.67	0.05	-60.12	0.10	9.22	0.0304	8.8713	0	0	10.7853	11.2669	6.43
LV24	2/07/2014	-8.67	0.11	-59.56	0.54	9.80	0.0303	8.8823	0	0	10.773	11.2877	6.75
LV25	9/07/2014	-8.51	0.05	-59.64	0.45	8.46	0.0461	8.9247	0	0	10.8656	11.3897	7.35

SURFACE WATER SITE: AVON RIVER (AR), HAGLEY PARK

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
AR01	5/03/2014	-4.94	0.05	-22.23	0.28	17.27	0.0288	12.1638	0.014	0.0228	2.794	6.0432	6.08
AR02	6/03/2014	-8.42	0.01	-56.98	0.76	10.34	0.0442	12.3266	0.046	0.0109	8.393	12.3324	6.68
AR03	7/03/2014	-8.78	0.05	-59.00	0.26	11.20	0.0473	13.1734	0.0006	0.0378	8.8704	11.4251	6.88
Avon @ Hagley March 8, 2014	8/03/2014	-8.77	0.03	-60.28	0.19	9.91							
AR04	13/03/2014	-8.96	0.04	-60.65	0.15	10.99	0.0476	12.3323	0	0.0179	9.2805	10.9697	6.76
AR05	15/03/2014	-8.95	0.01	-60.84	0.03	10.74	0.0428	11.3105	0	0.0188	9.4476	10.8871	6.79
AR06	16/03/2014	-4.32	0.05	-25.54	0.01	9.05	0.0179	6.477	0.0901	0.0023	2.522	4.3534	6.25
AR07	17/03/2014	-8.07	0.04	-56.57	0.37	7.98	0.0412	11.4285	0.0278	0.0157	7.5099	10.6344	6.75
AR08	18/03/2014	-8.63	0.06	-60.17	0.21	8.85	0.0448	11.6834	0	0	9.4075	11.3074	6.87
AR09	19/03/2014	-8.70	0.02	-60.72	0.14	8.90	0.0461	12.6528	0	0	9.3492	11.1192	6.96
AR10	26/03/2014	-8.51	0.12	-59.67	0.38	8.44	0.0388	11.6446	0.0089	0.0179	8.6828	10.6019	6.76
AR11	2/04/2014	-8.66	0.06	-60.02	0.04	9.23	0.0359	11.3303	0	0	9.5108	11.0499	6.92
AR12	9/04/2014	-8.52	0.01	-59.76	0.65	8.43	0.0281	11.1472	0.0182	0.0177	8.8723	11.1559	6.59
AR13	17/04/2014	-8.49	0.04	-61.19	0.45	6.71	0.0353	11.6838	0.015	0	9.5919	11.3634	6.83
AR14	23/04/2014	-8.60	0.07	-59.09	0.45	9.68	0.0354	11.9518	0.022	0.0213	9.42	12.2635	6.83
AR15	30/04/2014	-8.40	0.14	-58.12	0.66	9.07	0.0538	13.3243	0.0055	0.0228	9.2294	13.8183	6.71
AR16	7/05/2014	-8.70	0.10	-61.09	0.79	8.50	0.0319	11.8658	0.0046	0.0168	9.8413	12.3756	6.81
AR17	14/05/2014	-12.22	0.10	-88.64	0.44	9.09	0.0236	5.7157	0.009	0.0065	4.2349	5.8107	6.43
AR18	21/05/2014	-8.93	0.04	-61.03	0.30	10.40	0.0448	11.8763	0	0.0221	10.2317	12.565	6.7
AR19	28/05/2014	-9.21	#DIV/0!	-59.35	#DIV/0!	14.36	0.0323	11.6134	0	0	10.3772	12.3916	7.31
AR20	4/06/2014	-8.74	0.08	-61.28	0.90	8.64	0.0434	11.4511	0.0028	0.0166	10.2358	12.2908	7.24
AR21	11/06/2014	-8.49	0.05	-58.06	0.26	9.88	0.0279	11.8259	0	0	9.5989	12.7307	6.9
AR22	18/06/2014	-9.87	0.06	-72.36	0.71	6.62	0.0284	9.5634	0	0	7.7859	10.1021	6.55
AR23	25/06/2014	-8.63	0.02	-61.22	0.33	7.86	0.032	11.1956	0	0	9.8387	12.3853	6.75
AR24	2/07/2014	-8.67	0.01	-61.23	0.22	8.11	0.0309	11.2863	0	0	9.8586	12.0159	6.79
AR25	9/07/2014	-8.59	0.07	-61.60	0.67	7.16	0.0229	11.082	0	0	9.9119	12.0485	7.15

RAINWATER COLLECTION SITE: WESTERN SIDE OF VON HAAST BUILDING (GEO)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
GEO01	5/03/2014	-2.46	0.03	-5.89	0.45	13.79	0.016	12.9133	0.003	0.0281	0.5515	2.8939	6.06
GEO06	17/03/2014	-3.65	0.05	-25.52	0.68	3.70	0.0089	8.7897	0.0243	0.0201	0.27	1.6572	5.6
GEO10	26/03/2014	-6.53	0.07	-43.96	0.24	8.29	0.0115	10.451	0.051	0.0144	1.3862	2.5642	5.89
GEO12	8/04/2014	-5.08	0.06	-36.20	0.26	4.41	0.0042	1.2467	0.0256	0	0.4985	0.8802	5.47
GEO12A	10/04/2014	-5.64	0.02	-38.56	0.51	6.59							
GEO13	17/04/2014	-4.74	0.11	-32.49	0.25	5.45	0.0113	9.8621	0.0811	0	0.9772	3.29	5.6
GEO13A	19/04/2014	-5.68	0.09	-35.39	0.58	10.06							
GEO14	23/04/2014	-4.83	0.03	-25.83	0.13	12.83	0.0016	1.445	0.024	0	0.3325	0.4749	5.55
GEO15	28/04/2014	-11.19	0.07	-84.10	0.30	5.42							
GEO15A	29/04/2014	-8.28	0.08	-56.05	0.40	10.19	0	4.761	0	0	0.0405	0.6849	5.12
GEO15B	30/04/2014	-4.59	0.04	-24.73	0.42	12.03							
GEO17	14/05/2014	-11.42	0.04	-79.93	0.04	11.41	0.0251	1.3491	0.0225	0	0.473	1.3059	5.38
GEO19	26/05/2014	-8.35	0.03	-46.76	0.92	20.06	0.1807	12.0908	0.0324	0	2.1146	3.5043	6
GEO21	9/06/2014	-5.00	0.09	-34.18	1.02	5.83	0.1186	7.8416	0.1082	0	2.3412	3.1917	6.28
GEO21A	10/06/2014	-4.92	0.01	-25.02	#DIV/0!	14.32	0.0076	0.5322	0.0102	0	0.0791	0.4224	5.97
GEO21B	12/06/2014	-3.48	0.07	-12.90	0.19	14.93	0.1136	7.4133	0.0216	0	0.2011	1.8289	5.72
GE22	18/06/2014	-14.39	0.10	-111.14	0.30	3.98	0.0083	1.71	0.0317	0	0.5813	1.5271	6.07
GEO23	30/06/2014	-6.36	0.10	-54.92	0.41	-4.02	0.0035	4.7813	0.0455	0	1.1567	1.5345	6.04
GEO24	3/07/2014	-10.79	0.09	-77.40	0.26	8.95	0.1095	7.2104	0.053	0	2.5543	4.1782	5.9
GEO25	14/07/2014	-1.87	0.12	-2.97	0.52	12.02	0.1644	10.3679	0.0391	0	1.5769	3.8286	6.17

RAINWATER COLLECTION SITE: TOP OF PUAKA-JAMES HIGHT LIBRARY (JH)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
JH06	17/03/2014	-3.33	0.03	-16.79	0.25	9.84	0.0191	5.2412	0.0135	0	0.5546	1.6063	6.12
JH10	26/03/2014	-7.97	0.08	-53.25	0.10	10.54	0.0105	18.3838	0.0242	0.0198	0.9903	4.5394	5.73
JH12	9/04/2014	-5.07	0.06	-34.93	0.59	5.64	0.0041	3.1529	0.0283	0	0.667	1.5754	5.74
JH12A	9/04/2014	-5.72	0.03	-39.13	0.43	6.61							
JH14	23/04/2014	-6.71	0.07	-44.45	0.33	9.25	0.003	5.3763	0.0225	0	0.2053	1.4331	5.93
JH15	28/04/2014	-11.52	0.07	-85.83	0.31	6.33							
JH15A	29/04/2014	-8.10	0.05	-54.72	0.38	10.09	0	4.8928	0	0	0.0272	0.734	5.6
JH15B	30/04/2014	-4.50	0.07	-24.08	0.74	11.92							
JH17	14/05/2014	-11.05	#DIV/0!	-76.26	#DIV/0!	12.12	0.0313	3.809	0.0299	0	0.5591	2.4739	5.73
JH19	28/05/2014	-8.17	0.00	-44.79	0.28	20.54	0.527	26.9197	0	0	3.207	7.7291	6
JH21	9/06/2014	-4.72	0.06	-33.20	0.47	4.58	0.2691	29.0219	0.0884	0	3.8531	8.292	6.34
JH21A	10/06/2014	-5.21	#DIV/0!	-28.55	#DIV/0!	13.15	0	0.6464	0	0	0.0694	0.5414	6.11
JH21B	12/06/2014	-3.53	0.00	-13.29	0.61	14.94	0.1895	8.5341	0.0225	0	0.2568	2.4929	6.07
JH21B	12/06/2014	-3.33	0.08	-11.01	0.85	15.66							
JH22	18/06/2014	-14.38	0.09	-112.31	0.30	2.74	0.2666	10.1571	0.0262	0	1.0987	4.0947	6.66
JH23	30/06/2014	-6.36	0.10	-55.08	0.60	-4.18	0.2744	26.2789	0	0	2.5582	7.1851	5.63
JH24	3/07/2014	-10.60	0.10	-75.80	0.31	9.02	0.135	19.0623	0.0208	0	3.0803	6.0971	6.27
JH25	14/07/2014	-2.05	0.10	-4.09	0.48	12.27	0.3576	19.603	0.0281	0	2.5646	7.5985	6.18

RAINWATER COLLECTION SITE: ENGINEERING BLOCK DOWNPIPE (EN)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
EN01	5/03/2014	-1.27	0.06	-2.54	0.46	7.64	0.0428	11.7459	0	0.0204	3.6457	5.1605	5.63
EN06	16/03/2014	-4.51	0.07	-32.80	0.50	3.30	0.0011	1.4312	0	0	0.0218	0.2822	5.62
EN12	8/04/2014	-3.17	0.06	-16.30	0.19	9.07	0.006	0.6284	0.0304	0	0.097	0.9849	5.58
EN15	29/04/2014	-3.98	0.06	-20.74	0.38	11.09	0.0117	6.4661	0	0.0132	0.014	0.9628	5.55
EN17	14/05/2014	-5.86	0.03	-42.92	0.24	3.96	0.0142	1.0137	0.0333	0	0.1255	1.4986	5.58
EN17	14/05/2014	-5.72	0.05	-42.21	0.51	3.53							
EN25	9/07/2014	-2.05	0.03	-6.01	0.69	10.37	0.0084	1.5517	0.0574	0	0.1726	1.6583	6.03

RAINWATER COLLECTION SITE: TRAVIS HORTON EX-TROPICAL CYCLONE LUSI SAMPLES

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	Time of collection
Lusi - Rain	16/03/2014	-3.16	0.04	-14.05	0.12	11.21	9:40
Lusi - Rain	16/03/2014	-3.55	0.09	-14.76	0.41	13.61	9:40
Lusi - Rain	16/03/2014	-1.36	0.03	-1.12	0.15	9.77	11:45
Lusi - Rain	16/03/2014	-2.27	0.03	-6.71	0.24	11.43	11:45
Lusi - Rain	16/03/2014	-0.61	0.04	1.92	0.31	6.83	14:00
Lusi - Rain	16/03/2014	-1.66	0.08	-3.04	0.21	10.24	14:00
Lusi - Rain	16/03/2014	-2.25	0.03	-10.20	0.29	7.80	16:00
Lusi - Rain	16/03/2014	-3.41	0.06	-21.89	0.29	5.38	16:00
Lusi - Rain	16/03/2014	-1.87	0.08	-10.27	0.70	4.67	20:00
Lusi - Rain	17/03/2014	-2.81	0.05	-15.93	0.38	6.51	8:00
Lusi - Rain	17/03/2014	-3.50	0.07	-22.29	0.47	5.74	10:00

SURFACE WATER RESPONSE TO RAINFALL SITE: WAIMAIRI STREAM (WM)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
WM01	4/07/2014	-8.75	0.05	-61.06	0.23	8.96	0.0336	11.4159	0	0	11.2347	14.4741	6.37
WM02	5/07/2014	-8.75	0.04	-61.41	0.29	8.59	0.0419	11.4157	0	0	11.2799	14.4733	6.43
WM03	5/07/2014	-8.77	0.00	-61.79	0.76	8.39	0.0396	11.5567	0	0	11.4477	14.4816	6.39
WM04	5/07/2014	-8.70	0.04	-61.28	0.38	8.28	0.0372	11.3884	0	0	11.2622	14.3581	6.39
WM05	6/07/2014	-8.73	0.04	-61.08	0.16	8.78	0.0324	11.5159	0	0	11.3649	14.4332	6.34
WM06	6/07/2014	-8.56	0.07	-60.81	0.59	7.67	0.0339	11.6933	0	0	11.3641	14.4168	6.38
WM07	8/07/2014	-8.64	0.05	-60.56	0.31	8.53	0.0344	11.4266	0	0	11.392	14.4153	6.21
WM08	8/07/2014	-8.71	0.05	-60.75	0.25	8.94	0.0339	11.4159	0	0	11.3686	14.4055	6.44
WM09	9/07/2014	-8.71	0.06	-61.09	0.22	8.61	0.0388	11.6242	0	0	11.5626	14.5282	6.5
WM10	9/07/2014	-8.63	0.08	-59.87	0.10	9.19	0.0374	11.6046	0	0	11.1736	14.2253	6.37
WM11	9/07/2014	-6.73	0.09	-43.15	0.32	10.67	0.0351	11.1813	0	0	8.1162	10.8295	6.28
WM12	10/07/2014	-8.54	0.08	-59.65	0.12	8.68	0.0394	11.4573	0	0	11.1907	14.1663	6.36
WM13	10/07/2014	-8.65	0.11	-61.40	0.28	7.82	0.0912	11.5141	0	0	11.3931	14.4059	6.39
WM14	10/07/2014	-8.63	0.12	-60.82	0.22	8.19	0.0619	11.491	0	0	11.5828	14.4561	6.47
WM15	11/07/2014	-8.73	0.07	-61.25	0.16	8.61	0.0356	11.6572	0	0	11.3737	14.3639	6.68

SURFACE WATER RESPONSE TO RAINFALL SITE: OKEOVER STREAM (WM)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
OK01	4/07/2014	-8.70	0.13	-61.21	0.34	8.38	0.035	11.6302	0	0.0203	12.9326	10.307	6.33
OK02	5/07/2014	-8.74	0.07	-61.37	0.25	8.55	0.036	12.086	0	0.0226	13.2079	10.5569	6.3
OK03	5/07/2014	-8.70	0.11	-61.40	0.43	8.20	0.0571	11.5531	0	0	12.9177	10.2474	6.33
OK04	5/07/2014	-8.68	0.05	-61.35	0.43	8.07	0.0355	11.05045	0	0	12.8759	10.2142	6.34
OK05	6/07/2014	-8.63	0.02	-61.28	0.41	7.78	0.0371	11.5357	0	0.0219	12.9867	10.2934	6.35
OK06	6/07/2014	-8.68	0.11	-60.90	0.30	8.55	0.037	11.7133	0	0.0144	13.006	10.3069	6.35
OK07	8/07/2014	-8.65	0.07	-61.08	0.16	8.13	0.0361	11.4659	0	0.0259	12.9119	10.2767	6.41
OK08	8/07/2014	-8.55	0.02	-61.62	0.49	6.81	0.0366	11.5629	0	0.0218	13.0681	10.3307	6.39
OK09	9/07/2014	-8.71	0.08	-61.05	0.25	8.60	0.036	11.5445	0	0	13.0277	10.2608	6.42
OK10	9/07/2014	-8.61	0.06	-60.74	0.60	8.12	0.0377	11.637	0	0.0215	12.5246	10.3927	6.37
OK11	9/07/2014	-6.46	0.09	-41.02	0.15	10.64	0.0303	10.4014	0.0092	0.0178	8.5882	7.5702	6.24
OK12	10/07/2014	-8.66	0.08	-60.33	0.19	8.94	0.0416	11.5993	0	0.0205	12.9616	10.2118	6.42
OK13	10/07/2014	-8.65	0.05	-61.14	0.13	8.08	0.0372	11.5243	0	0.0231	13.0265	10.3138	6.39
OK14	10/07/2014	-8.68	0.05	-61.05	0.06	8.36	0.0341	11.5534	0	0.0219	13.1051	10.2917	6.5
OK15	11/07/2014	-8.59	0.05	-61.13	0.29	7.58	0.0291	11.6744	0	0.0367	13.0433	10.3429	6.45

SURFACE WATER RESPONSE TO RAINFALL SITE: AVON RIVER (AV)

Sample Code	Date Collected	Corrected $\delta^{18}O$	$\delta^{18}O$ StDev (4 injections)	Corrected δD	δD StDev (4 injections)	d-excess	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	pH
AV01	4/07/2014	-8.45	0.20	-59.74	0.48	7.84	0.0406	13.7516	0	0	14.9392	14.0696	6.4
AV02	5/07/2014	-8.61	0.03	-59.85	0.27	9.06	0.062	13.7347	0	0	14.9369	14.0422	6.27
AV03	5/07/2014	-8.64	0.06	-60.88	0.42	8.28	0.0582	13.7948	0	0	14.9815	13.9522	6.39
AV04	5/07/2014	-8.66	0.04	-61.22	0.48	8.02	0.0355	14.0228	0	0	15.1275	14.0539	6.33
AV05	6/07/2014	-8.67	0.08	-60.80	0.28	8.52	0.1033	13.6714	0	0	14.9745	13.9209	6.39
AV06	6/07/2014	-8.62	0.01	-60.74	0.15	8.24	0.1306	13.7931	0	0	14.9989	13.8706	6.32
AV07	8/07/2014	-8.61	0.06	-60.82	0.40	8.05	0.0338	13.5319	0	0	14.6562	13.7079	6.39
AV08	8/07/2014	-8.61	0.01	-60.33	0.17	8.53	0.0349	13.6063	0.0075	0.0266	14.8055	13.8084	6.59
AV09	9/07/2014	-8.72	0.08	-61.15	0.15	8.61	0.0303	13.5195	0	0	14.6198	13.7625	6.54
AV10	9/07/2014	-8.31	0.04	-57.84	0.53	8.68	0.0289	13.6264	0.0137	0	13.9894	13.3783	6.44
AV11	9/07/2014	-5.94	0.10	-36.96	0.35	10.59	0.0273	11.9778	0.0086	0.023	8.7052	9.2793	6.35
AV12	10/07/2014	-7.97	0.04	-55.01	0.23	8.72	0.0465	13.5227	0.0124	0.0258	13.5803	12.9897	6.46
AV13	10/07/2014	-8.51	0.10	-59.62	0.67	8.44	0.037	13.7683	0	0.0302	14.6842	13.959	6.46
AV14	10/07/2014	-8.59	0.07	-60.24	0.42	8.49	0.0356	13.8395	0.117	0.0292	14.7444	13.9857	6.5
AV15	11/07/2014	-8.57	0.08	-60.03	0.13	8.54	0.0365	13.8544	0.0135	0.0291	14.7246	13.859	6.5

SITE COORDINATES (REFERENCE: GOOGLE EARTH, IMAGE TAKEN 26 APRIL, 2012)

SITE LOCATION	SITE CODE	SOUTHING COORDINATE	EASTING COORDINATE
Waimakariri River	**WK**	43° 26′ 44.53″	172° 30′ 31.84″
Chattertons Rd (North)	**MN**	43° 28′ 32.11″	172° 26′ 31.84″
Chattertons Rd (South)	**MS**	43° 29′ 15.83″	172° 25′ 56.93″
Avonhead Park	**AP**	43° 30′ 41.59″	172° 32′ 22.21″
Okeover Stream, University of Canterbury	**UC**	43° 31′ 20.24″	172° 35′ 03.99″
Lake Victoria	**LV**	43° 31′ 38.23′	172° 37′ 15.14″
Avon River, Hagley Park	**AR**	43° 31′ 41.20″	172° 37′ 12.36″
Puaka-James Hight Library, University of Canterbury	**JH**	43° 31′ 25.49″	172° 34′ 57.94″
Von Haast Building, University of Canterbury	**GEO**	43° 31′ 20.01″	172° 34′ 59.69″
Engineering Block, University of Canterbury	**EN**	43° 31′ 18.84″	172° 35′ 00.03″
Waimairi Stream, Clyde Rd	**WM**	43° 31′ 18.84″	172° 35′ 23.11″
Okeover Stream, Clyde Rd	**OK**	43° 31′ 23.28″	172° 35′ 14.59″
Avon River, Clyde Rd	**AV**	43° 31′ 35.76″	172° 35′ 12.60″

APPENDIX III: ADDITIONAL GRAPHS

Figure A: Presents fluctuations of anion concentrations obtained from rainwater samples over the sample period. Consists of the compilation of EN, JH, & GEO rain water samples. Note separate axes used for chloride, sulfate and nitrate, and nitrite, fluoride & bromide. Blue bars in the background correlate to daily rainfall values on right-hand inner axis.